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Melissa Ann Manuszak guerrini

Louisiana State University and Agricultural & Mechanical College

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**CHARACTERIZATION OF
AMINOALKYLCARBAMOYL CELLULOSIC AND CHITOSAN
DERIVATIVES FOR USE IN COSMETIC FORMULATION**

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy**

in

The Department of Chemistry

by

**Melissa Ann Manuszak Guerrini
B.S., Miami University, Oxford, 1991
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August 1997**

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DEDICATION

To my husband, Vincent, for all his love and support

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I wish to express my sincere appreciation to my major Professor, Dr. William H. Daly, for his guidance and encouragement of this new project. For his advice, patience and support, I am deeply grateful. Dr. Robert Y. Lochhead, my minor advisor, deserves special thanks. His wealth of knowledge of polymer - surfactant interactions and cosmetics has been invaluable to this project. I would like to thank Dr. Nikolaus H. Fischer, Dr. Paul S. Russo, Dr. Judith A. Schiebout and Dr. Isiah M. Warner for serving as my committee members, for their advice and suggestions.

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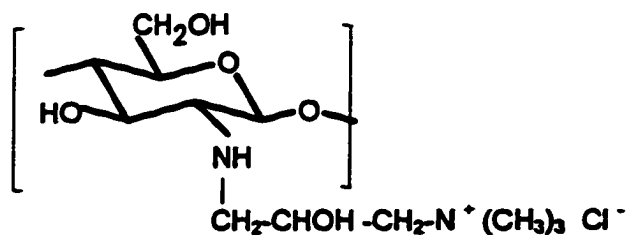
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ABBREVIATIONS

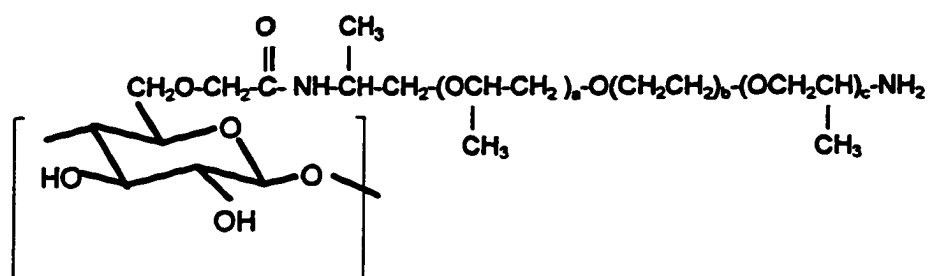
CHI-Q188

hydroxypropyl trimethylammonium chitosan chloride



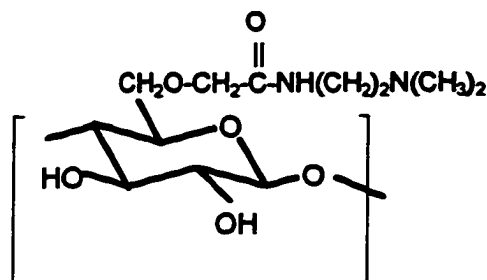
CMCJ600

Carbamoylmethylcellulose-g-co-(polyoxyethylene-polyoxypropylene)-amine



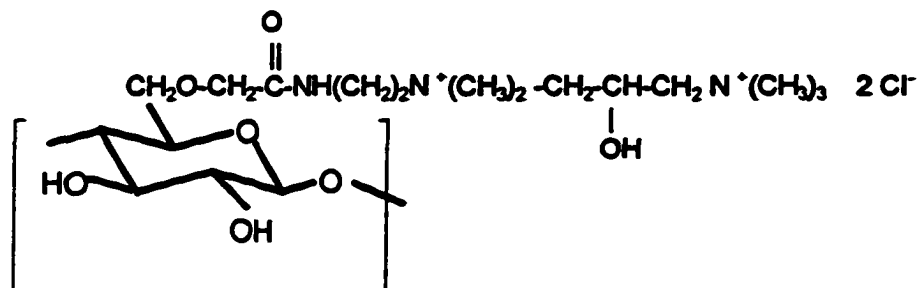
CMCNED

N,N-dimethylaminoethylcarbamoylmethyl cellulose



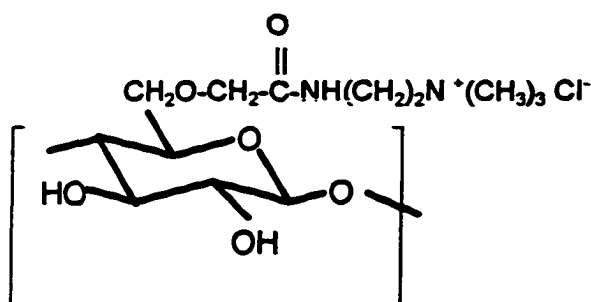
DQNNED

3-trimethylammonium-2-hydroxypropyl-n-N,N-dimethylammoniummethyl carbamoylmethyl cellulose chloride



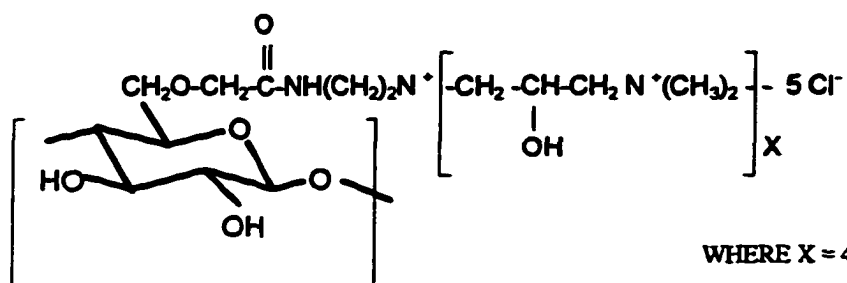
MQNNED

2-trimethylammoniummethylcarbamoylmethyl cellulose chloride



PQNNED

N,N-dimethylammoniummethyl carbamoylmethyl cellulose-g-co-(poly-N'-3-trimethylammonium-2-hydroxypropyl) chloride



WHERE X = 4 OR 5

| | |
|--------------------------|--|
| β | beta |
| Γ | average decay rate (Chapter 7); surface tension (Chapter 8) |
| γ | shear rate |
| ϵ | molar absorptivity |
| η | viscosity |
| η_{int} | intrinsic viscosity |
| $\eta_{\text{int, app}}$ | apparent intrinsic viscosity |
| η_{rel} | relative viscosity |
| η_{solution} | viscosity of the solution |
| η_{solvent} | viscosity of the solvent |
| η_{sp} | specific viscosity |
| θ | scattering angle |
| λ | wave length |
| μm | micrometers |
| μM | micromoles |
| ξ | polymer linear charge density |
| σ | force per unit area (Chapter 2); micelle surface charge density (Chapter 6) |
| \leq | less than or equal to |
| \geq | greater than or equal to |
| $<$ | less than |
| $>$ | greater than |

| | |
|--------------------|---|
| $1/b$ | structural polymer charge density |
| $^{\circ}\text{C}$ | degrees Celsius |
| A | area |
| APC | aerobic plate count |
| c | concentration |
| c^* | critical overlap concentration |
| c^*_{app} | apparent critical overlap concentration |
| CAC | critical aggregation concentration |
| CFC | chlorofluorocarbons |
| cm | centimeters |
| C_M | total monomer concentration at equilibrium |
| CMC | critical micelle concentration |
| CMCamide | aminoalkylcarbamoyl methylcellulose |
| CMC_A | critical micelle concentration of species A |
| CMC_B | critical micelle concentration of species B |
| CP | cloud point |
| C_s | total surfactant concentration |
| Dansyl-BA | <i>m</i> -dansylaminophenyl boronic acid |
| DLS | Dynamic Light Scattering |
| D_m | mutual diffusion coefficient |
| DS | degree of substitution |
| <i>E. coli</i> | <i>Escherichia coli</i> |

| | |
|-----------------|---|
| E_v | activation energy |
| exp | exponential |
| F | force |
| $g^{(1)}(q, t)$ | first order electric field autocorrelation function |
| $g^{(2)}(q, t)$ | homodyne intensity autocorrelation function |
| HCl | hydrochloric acid |
| HPC | hydroxypropylcellulose |
| I | ionic strength |
| I_1 | pyrene fluorescence band at 372 nm |
| I_3 | pyrene fluorescence band at 383 nm |
| Jeffamine 600 | g-co-(polyoxyethylene-polyoxypropylene)-amine |
| k | Boltzmann constant |
| K^{-1} | Debye-Hückel ion atmosphere thickness |
| kV | kilovolts |
| lim | limit |
| L | liter |
| L/G | liquid/gas interface |
| LMM | low molar mass |
| <i>m-</i> | <i>meta</i> |
| mM | millimoles |
| mol | moles |
| M | molarity |

| | |
|-----------------------------|---|
| MCMC | methylcarboxymethyl cellulose ester |
| MIC | minimum inhibitory concentration |
| MPCP | minimum possible cloud point |
| MPST | minimum possible sterilization time |
| MW | molecular weight |
| n | refractive index |
| NaCl | sodium chloride |
| NaCMC | carboxymethylcellulose, sodium salt |
| NaOH | sodium hydroxide |
| nm | nanometers |
| NMR | Nuclear Magnetic Resonance |
| NNED | N,N',-dimethylethylene diamine |
| <i>o</i>- | <i>ortho</i> |
| OD | optical density |
| <i>p</i>- | <i>para</i> |
| <i>P. aeruginosa</i> | <i>Pseudomonas aeruginosa</i> |
| PET | Preservative Efficacy Test |
| polyquat(s) | polyquaternary ammonium salt(s) |
| q | wave vector |
| Quat 188 | hydroxypropyl trimethylammonium chloride |
| quats | quaternary ammonium compounds |
| R | Gas constant |

| | |
|------------------|--|
| <i>S. aureus</i> | <i>Staphylococcus aureus</i> |
| SDS | sodium dodecyl sulfate |
| SEM | Scanning Electron Microscopy |
| ST | sterilization time |
| $t_{1/2}$ | half-life |
| T | absolute temperature |
| T_K | Krafft point |
| u | velocity |
| VOC | volatile organic compounds |
| w/v | weight per volume |
| X_A | micellar mole fraction of species A |
| X_B | micellar mole fraction of species B |
| Y | mole fraction of ionic surfactant |
| Y_A | mole fraction of species A |
| Y_B | mole fraction of species B |
| Y_C | critical mole fraction of ionic surfactant |
| Y_{SDS} | mole fraction of charged monomers |

ABSTRACT

Polymer and surfactant interactions have been a subject of intense research due to industrial applications utilizing a polymer-surfactant system, such as cosmetic formulation. A series of aminoalkylcarbamoyl cellulose derivatives were prepared from the amidation of methylcarboxymethyl cellulose. These derivatives were quaternized with either iodomethane, or hydroxypropyl trimethylammonium chloride, or epichlorohydrin and dimethylamine to yield polyquaternary ammonium salts. The focus of this dissertation is the characterization of a family of these compounds based on N,N',-dimethylethylene diamine. As these compounds are similar to Polyquaternium 10, a quaternized hydroxyethyl cellulose derivative, the solution properties have been characterized; antimicrobial activity and keratin affinity have been determined.

Viscosity measurements indicated that derivatives containing a low number of cationic charges per graft and shorter graft length have the highest viscosity. Solubility studies showed that the polymers precipitate at their respective theoretical charge neutralization ratios at concentrations of polymer and anionic surfactant greater than 0.010%. At low polymer concentrations, a fixed concentration of sodium dodecyl sulfate was necessary to precipitate the complexes. The critical mole fraction of anionic surfactant necessary to cause precipitation of polymer - mixed surfactant micelle complexes was dependent upon polymer flexibility, charge density and polymer concentration. Changes in pyrene fluorescence intensity indicated that the micellar regions formed in these complexes were more hydrophilic than free micelles. Dynamic light scattering showed that systems containing Polyquaternium 10 were nearly monodisperse; whereas, systems containing our polymers were polydisperse. The

Polyquaternium 10 - mixed surfactant micelle complex exhibited a different temperature response than complexes formed with the aminoalkylcarbamoyl cellulose derivatives. Surface tension studies showed evidence of three interaction zones which were present regardless of polymer structure or charge density. Foam studies indicated that the system containing Polyquaternium 10 required more polymer to produce maximal foamability of SDS than either of our polymers. Bactericidal activity of the polymers against *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* was determined. The results indicated that quaternary polymers may have a dual role in cosmetic products as preservatives and thickeners. Finally, scanning electron microscopy indicated that the binding of the polymers to the hair fibers was not uniform in all cases.

CHAPTER 1: LITERATURE REVIEW

1.1 CATIONIC POLYMERS

Polymeric quaternary ammonium salts (polyquats) have a variety of uses in cosmetic formulations due to their solubility in both aqueous and aqueous-alcoholic media. Polyquats have been used as thickeners, emulsifiers, fixatives or film formers, and as additives in formulations to improve combing of hair, manageability, body, curl retention and substantivity of ingredients to keratin.^{1,2} The particular application of a polymer depends on the polymer's ability to absorb at an interface, stabilize dispersions, emulsify, and confer the preferred rheology by means of a three dimensional network.² Cationic ingredients are substantive to hair keratin due to the low isoelectric point of hair (pH = 3.67).³ However, the high affinity of some cationic polymers has limited their use due to soiling (build up) and resistance to removal by anionic surfactants.¹

1.1.1 Chitosan

Chitin [poly β -(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose] is the major constituent in shells of crustaceans, such as shrimp, crab, or crawfish.⁴ This product (Figure 1.1) is obtained after the crushed shells are demineralized to extract the proteins and polypeptides.^{4,7} Chitin is the second most abundant biopolymer in nature⁷ and is a waste product of the seafood industry.⁸

Chitosan [poly β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucopyranose] is a natural biopolymer primarily composed of 2-amino-2-deoxy-D-glucose (D-glucosamine) and 2-acetamido-2-deoxy-D-glucose (N-acetyl-D-glucosamine) which are two common constituents of the body.⁷ This polycationic polymer (Figure 1.2) is obtained by alkaline deacetylation of chitin.^{4,7}

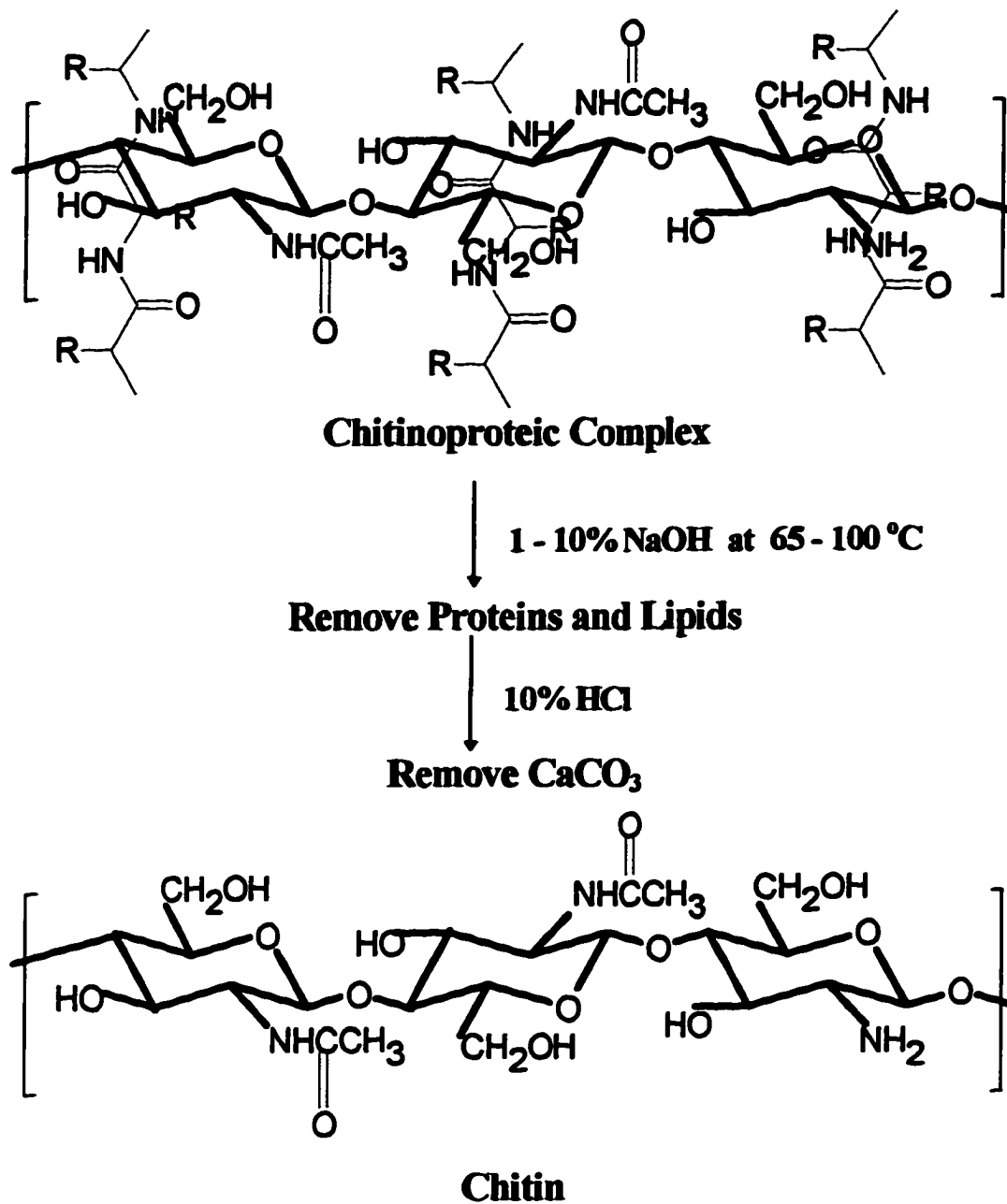


Figure 1.1: Isolation of Chitin.

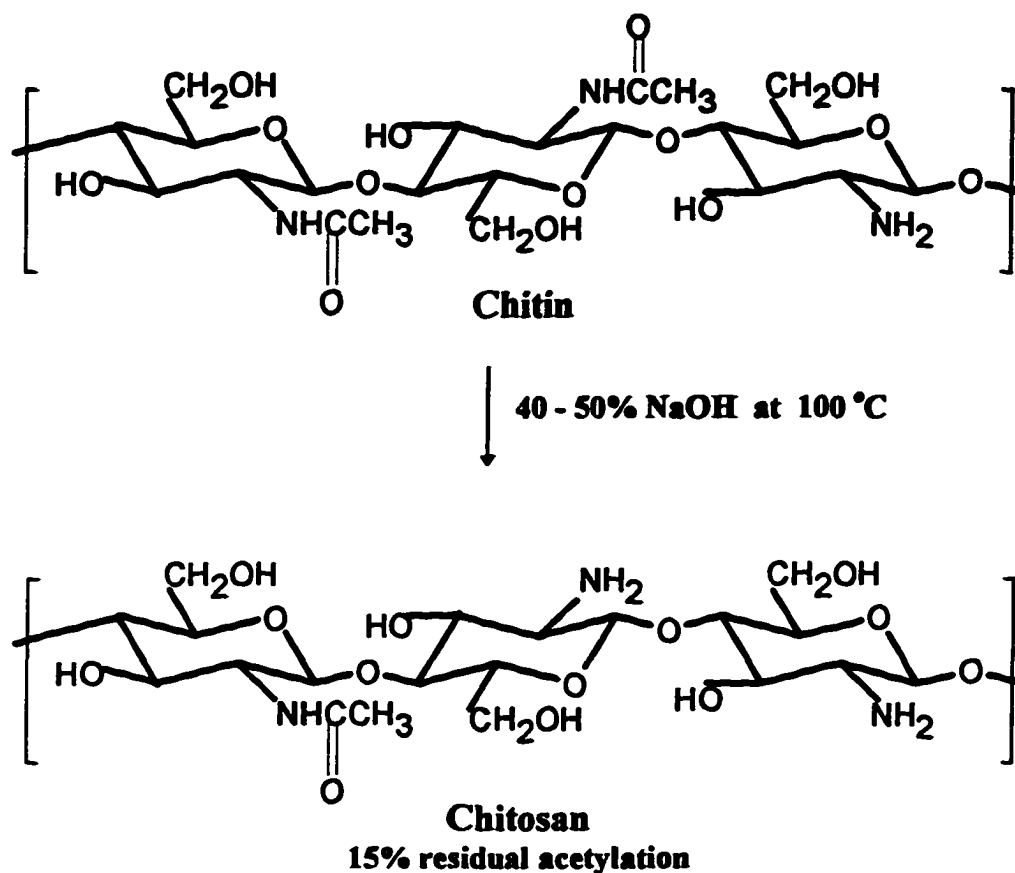


Figure 1.2: Isolation of Chitosan.

The important variable characteristics of chitosan are: the degree of deacetylation, molecular weight, solubility, and coagulating ability.⁴ The viscosity of solutions containing chitosan is affected by the degree of deacetylation, molecular weight, concentration, ionic strength, pH and temperature. Generally, increases in temperature cause decreases in the viscosity of the solution; whereas, the effect of pH on viscosity depends on the acid used. Native chitosan is soluble in organic acids when the

pH is less than 6 and insoluble in water, alkali or organic solvents.⁴ However, water soluble salts of chitosan may be formed by neutralization with hydrochloric acid, acetic acid, lactic acid, or formic acid.⁵ Chitosan has found many uses in different areas. These areas include water treatment,⁹⁻¹³ paper manufacturing,¹⁴⁻¹⁶ agriculture and food processing,¹⁷⁻²¹ cosmetics,²²⁻²⁹ biotechnology,³⁰⁻³⁴ and medicine.²²⁻²⁹

1.1.2 Cosmetic Applications of Chitosan Derivatives

Chitosan and its derivatives have been reportedly used as film formers in hair products,^{35,36} setting agents,³⁷ hair conditioners and shampoos.³⁸ However, the use of chitosan and chitosan salts in personal care products has been limited. The insolubility of chitosan derivatives in the solvent systems of these products, such as aqueous, neutral to alkaline solutions, or anionic detergents, is the cause of limited use.

Lang and coworkers have investigated the synthesis of water soluble chitin and chitosan derivatives (Figure 1.3) which might also be compatible with anionic detergents.³⁶ Reactions with epoxides such as ethylene oxide, propylene oxide,³⁹ butylene oxide and glycidol⁴⁰ were found to yield water soluble chitosan derivatives that were compatible with anionic detergents.⁵ Mixed epoxides such as ethylene oxide and glycidyltrimethylammonium chloride,⁴¹ propylene oxide,⁴² and glycidol⁴³ with cationic chitosans yielded derivatives capable of use in all cosmetic formulations; while substitution of short chain nonionic epoxides by long chain epoxides were found to yield derivatives with detergent properties.³⁶ Finally, chitosan was sulfoalkylated with 1,3-propane sultone to yield sulfopropyl substituted ampholytic or anionic derivatives.⁴⁴ These derivatives are thought to be well suited for use in hair products.

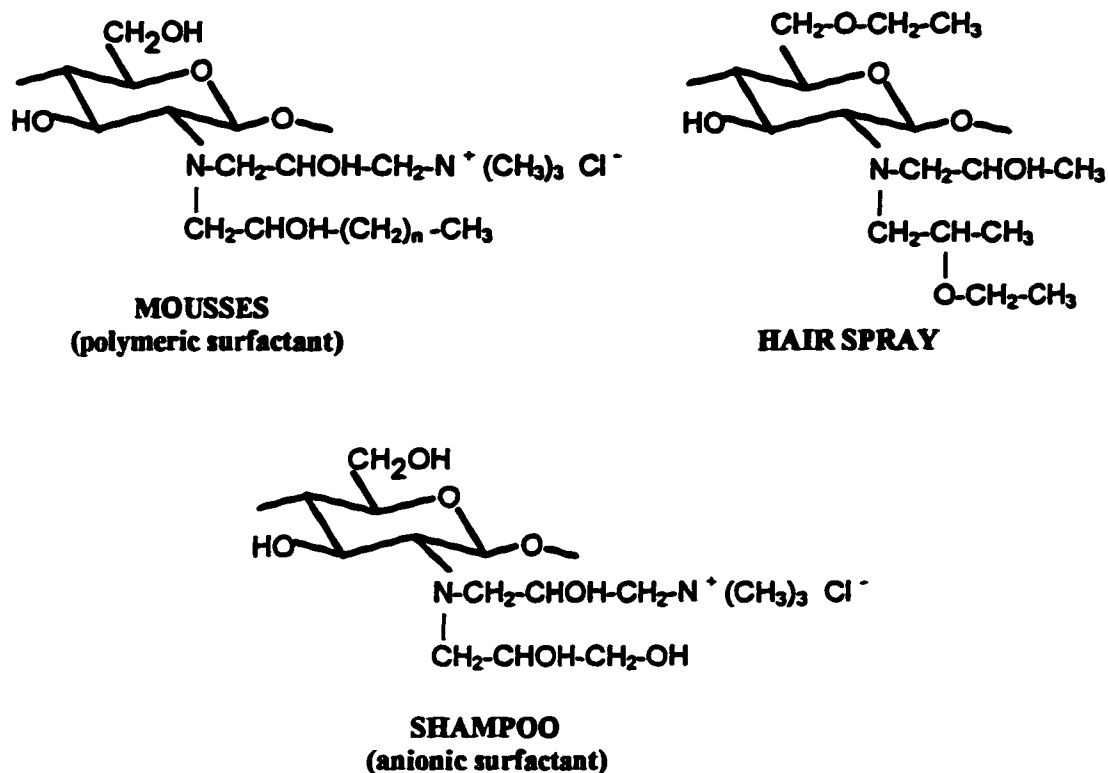


Figure 1.3: Chitosan Derivatives Synthesized for Cosmetic Applications.

The production of hydroxypropyl chitosan and hydroxypropyl trimethylammonium chitosan chloride^{45,46} has been the focus of a major research effort in the laboratories of W. H. Daly. Since these materials (Figure 1.4) have many potential applications in the cosmetic industry, the initial objective of this dissertation was the characterization of the solution properties and keratin affinities of these materials. However, the poor viscosity enhancing properties or poor compatibility with anionic surfactants prompted an extension of the study to include cationic cellulose derivatives.

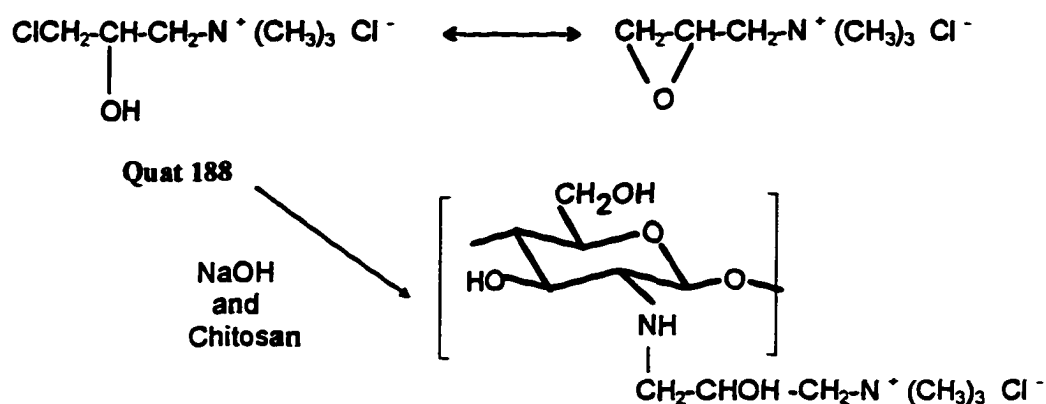
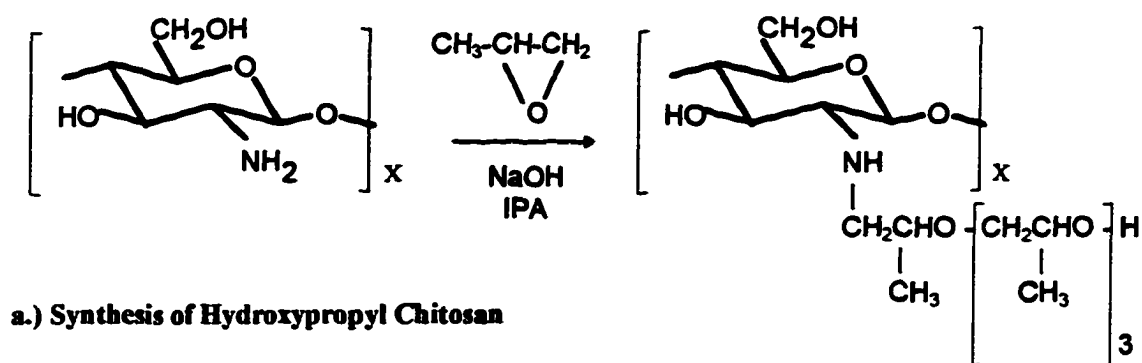


Figure 1.4: Hydroxypropyl Chitosan and Hydroxypropyl Trimethylammonium Chitosan Chloride.

1.1.3 Cellulose

Cellulose (Figure 1.5) is a natural biopolymer composed of [poly β -(1 \rightarrow 4)- D-glucose]. The numerous hydroxyl groups undergo extensive intra- intermolecular hydrogen bonding making it a stiff, rodlike polymer. Cellulose in its natural form contains amorphous and crystalline regions. Reactions generally occur in the amorphous regions first. Pretreatment with alkali activates the hydroxyl groups and facilitates the

formation of derivatives. The hydroxyl groups on carbons C2 and C3 are secondary alcohols and the hydroxyl group on carbon C6 is a primary alcohol (Figure 1.6). The rates of reactivity of the hydroxyl groups depend on the reagent used. For esterification reactions, the rates of reactivity are $C6 > C2, C3$; while for etherification reactions the reactivity rates are $C2 > C6 > C3$.⁴⁷⁻⁴⁹

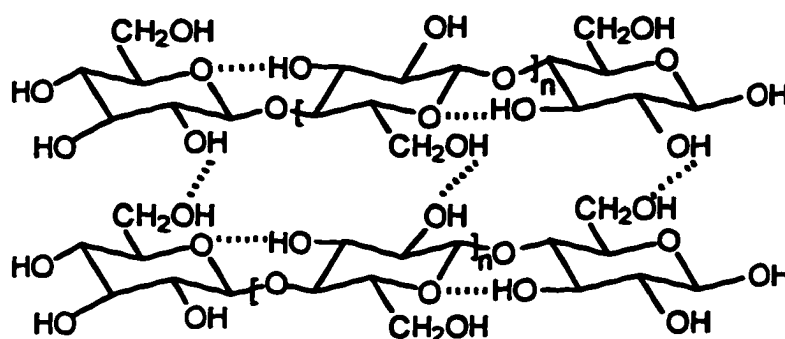


Figure 1.5: Cellulose.

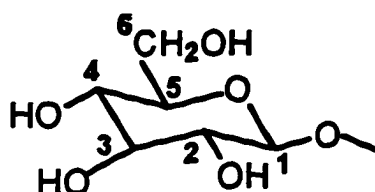


Figure 1.6: Position of Hydroxyl Groups on Cellulose.

The properties of cellulose derivatives are influenced by the degree of substitution along the cellulose chain. For cellulose, the degree of substitution is the average number of hydroxyl groups that have been substituted per anhydroglucose ring. The hydroxyl groups which may be substituted are located at the C2, C3, C6 positions on the anhydroglucose ring.

Cellulose derivatives are used in cosmetics as film formers for nail lacquers, skin and hair conditioners and gelling agents in toothpastes, to name a few applications. Their use is dependent upon the particular cellulose derivative and the modifications to the grafted substituent.

1.1.3.1 Polyquaternium 10

Polyquaternium 10 (Figure 1.7) is a quaternized hydroxyethyl cellulose polymer⁵⁰ formed from the alkaline reaction of hydroxyethylcellulose with epichlorohydrin followed by quaternization with trimethylamine. Approximately 1 cationic group per 2 anhydroglucose repeat units⁵¹ leads to a relatively low average molecular weight per cationic charge of approximately 670 g/mol.^{52,53} and a high density of polar groups.

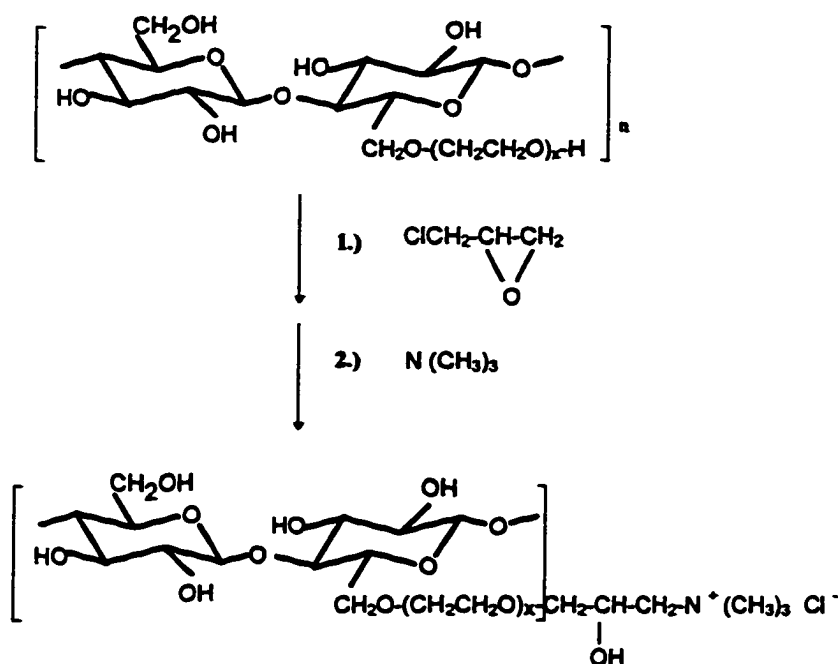


Figure 1.7: Structure of Polyquaternium 10.

Polyquaternium 10 is used in shampoos, conditioners, gels, mousses, and skin care products, such as lotions, moisturizers and cleansers.^{1,54} Due to the attributes imparted to hair, such as manageability and ease of combing, Polyquaternium 10 has been used frequently in shampoo formulations.⁵³

The binding interactions of polymers with hair keratin,^{55,56} rheological and flow properties of polymer solutions, film forming and adhesion properties⁵⁷⁻⁶⁰ have been evaluated. In particular, the effects of molecular weight, pH, charge, electrolyte interactions and surfactant interactions on behavior of Polyquaternium 10 has been studied in great detail by Goddard and Faucher.^{51-53,61,62}

The uptake of different molecular weight versions of Polyquaternium 10 onto bleached and virgin hair was studied by Faucher and Goddard using a radiotracer method.⁶¹ It was determined that the lowest molecular weight species was adsorbed the fastest and to the greatest extent. High molecular weight species showed rapid uptake of polymer followed by a leveling off which indicated saturation of the fiber surface. The effect of charge was studied by comparing Polyquaternium 10 (MW 250,000) with hydroxyethyl cellulose.⁶¹ The uptake of charged polymer was determined to be 50 times that of the uncharged hydroxyethyl cellulose polymer.^{1,61} Electrostatic attraction between the cationic groups of the polymer and the anionic sites of the hair fiber was determined to be the driving force.⁶²

The effect of pH was studied in unbuffered media at pH 4, 7, and 10.⁶¹ The amount of polymer adsorbed at pH 7 was greater than the amount adsorbed at either pH 4 or 10. At acid pH, the reduction in amount of polymer adsorbed was attributed to the

increasing positive charge on the hair fiber. Decreased sorption at alkaline pH was attributed to changes in structure of hair fibers at high pH.

Addition of electrolyte, sodium chloride, was found to decrease the amount of Polyquaternium 10 adsorbed by approximately 66%.⁵¹ This result was attributed to competition between the sodium ions and cationic polymer for the anionic sites on the hair fiber.⁶² Electrolytes having trivalent cations were found to decrease sorption by a greater extent than either divalent cations or monovalent cations.

It is well known that cationic polymer deposition is decreased when surfactants are included in a formulation, especially anionic surfactants.⁶³ All surfactants examined were determined to decrease the amount of polymer adsorbed onto the hair fiber regardless of surfactant charge.^{53,61} Both anionic and cationic surfactants were found to decrease the amount of polymer adsorbed greater than nonionic surfactants. It is hypothesized that the anionic surfactants decrease sorption by formation of association complexes with the polymer.¹ Cationic surfactants are hypothesized to decrease sorption by competitive inhibition.¹

The major drawback to the use of Polyquaternium 10 has been its low degree of desorption from keratin. Faucher *et al.*⁵¹ determined that less than 15% of Polyquaternium 10 was desorbed from hair by distilled water in 30 minutes. In a similar study,⁶² a 0.1M solution of sodium dodecyl sulfate (SDS) desorbed approximately 50% of the polymer in 1 minute and 70% in 30 minutes. However, a small amount of polymer still remained strongly bound to the hair fibers after further treatment with SDS.⁶² Salts were determined to be effective in the removal of Polyquaternium 10 from hair fibers.^{51,62} Trivalent salts were determined to be more effective than either divalent or monovalent

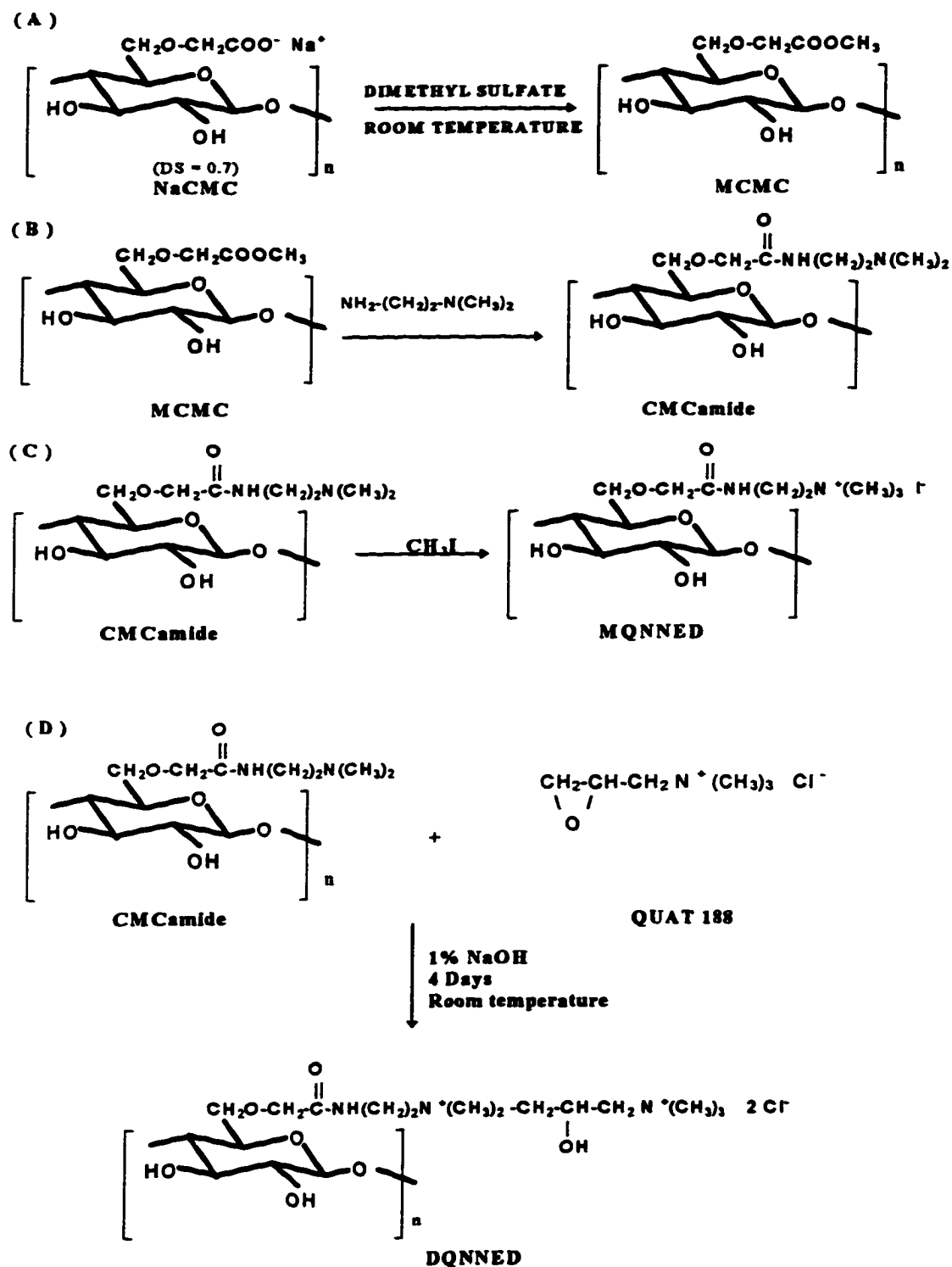
salts. However, both dilute salt solutions and deionized water were found to be less effective than 0.1 M SDS in desorbing Polyquaternium 10 from hair fibers.⁶² When sodium chloride and SDS were combined, no synergistic effect was observed on amount of polymer desorbed.

1.1.3.2 Aminoalkylcarbamoyl Cellulose Derivatives

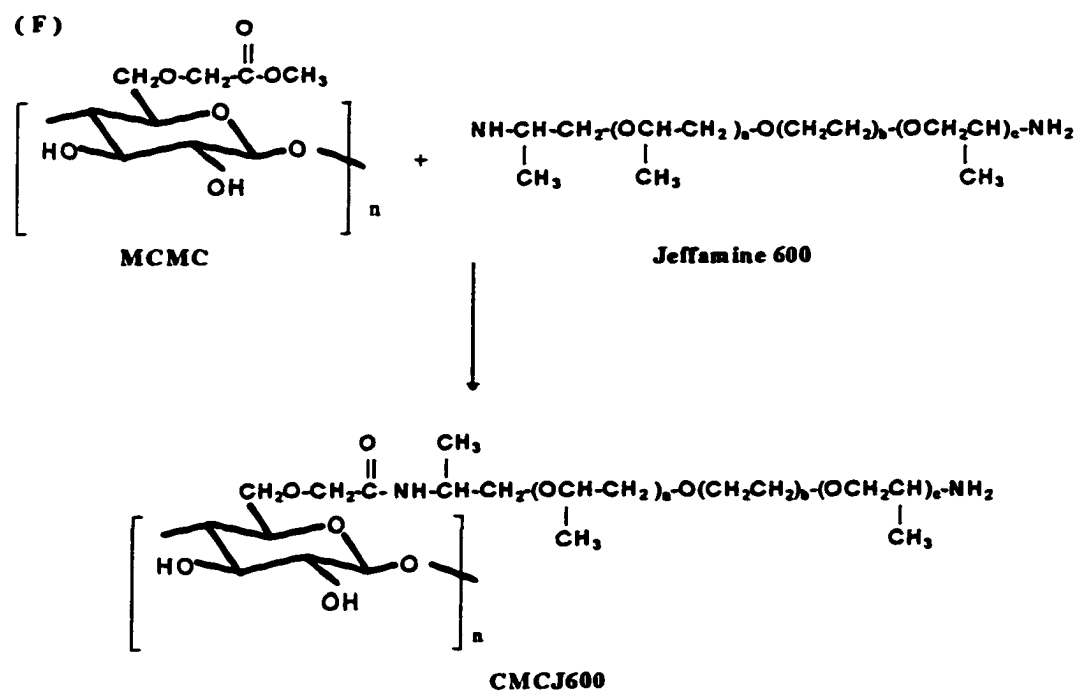
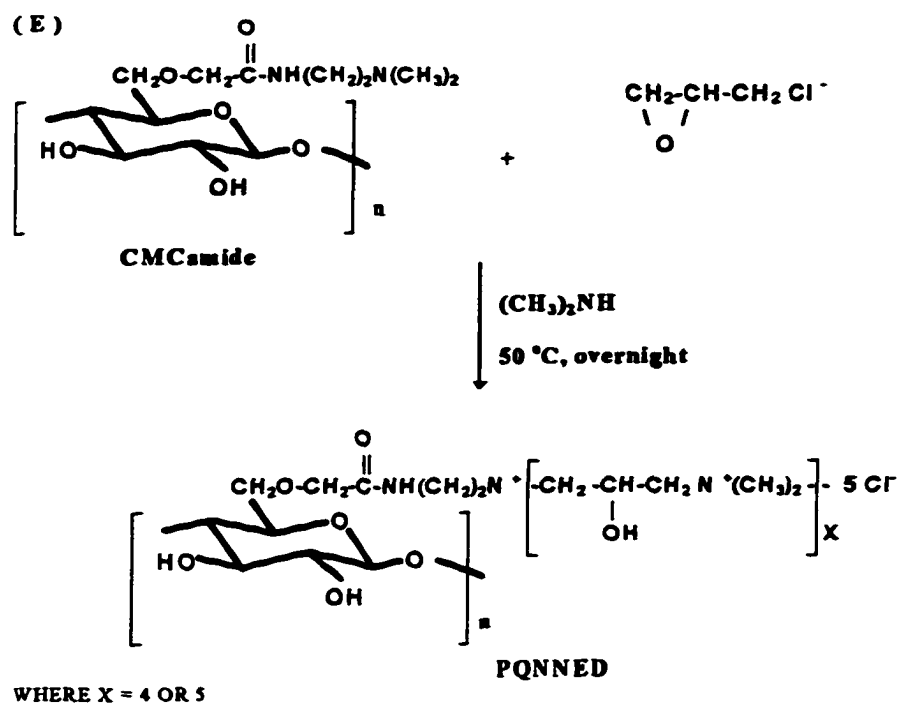
Due to the high cost of chitosan derivatives, the production of aminoalkylcarbamoyl cellulose derivatives⁶⁴⁻⁶⁶ has become the focus of a major research effort in the laboratories of W. H. Daly. Since these materials (Figure 1.8) which are similar to Polyquaternium 10 have many potential applications in the cosmetic industry, this dissertation will focus on the characterization of the solution properties and keratin affinities of these materials.

The aminoalkylcarbamoyl cellulose derivatives are formed by conversion of carboxymethylcellulose. Sodium carboxymethylcellulose (NaCMC) is converted to a water insoluble ester by reaction with neat dimethylsulfate (Figure 1.8A). The methyl carboxymethylcellulose ester (MCMC) reacts under homogeneous conditions with neat diamines, such as N,N',-dimethylethylene diamine (NNED), to yield water soluble aminoalkylcarbamoyl methylcelluloses (CMCamide) (Figure 1.8B). Quaternary ammonium salts of the aminoamide derivatives may then be prepared by reaction with iodomethane, hydroxypropyl trimethylammonium chloride (Quat 188), epichlorohydrin and dimethylamine, or g-co-(polyoxyethylene-polyoxypropylene)-amine (Jeffamine 600) to produce monoquaternary (MQNNED), diquaternary (DQNNED), polyquaternary (PQNNED) or Jeffamine derivatives (CMCJ600), respectively (Figure 1.8D-F).

Figure 1.8: Aminoalkylcarbamoyl Cellulose Derivatives
(A) Reaction of NaCMC to form MCMC ester
(B) Reaction of MCMC ester to form CMCamide
(C) Reaction of CMCamide to form MQNNED
(D) Reaction of CMCamide to form DQNNED
(E) Reaction of CMCamide to form PQNNED
(F) Reaction of CMCamide to form CMCJ600



(Figure continued)



As these aminoalkylcarbamoyl cellulose derivatives are similar to Polyquaternium 10, the focus of this dissertation will be the characterization of solution properties and keratin affinity of a family of these compounds namely those based upon the N,N',-dimethylethylene diamine (NNED) moiety. The study will include viscosity measurements, interactions with surfactants by solubility, pyrene fluorescence, dynamic light scattering, surface tension and foaming, bactericidal activity and keratin affinity by use of microscopy. The results of these studies will lend insight to the applicability of these derivatives in cosmetic formulations as thickeners, fixatives, conditioning agents, and preservatives.

CHAPTER 2: VISCOSITY

2.1 INTRODUCTION

Cationic polymers are used in the cosmetics, pharmaceutical and food industries as thickeners, gelling agents and dispersants. Their use and usage levels are ultimately determined by the change in the viscosity of the formulation. Therefore, the objective of this work is to determine the viscosity of aqueous solutions of quaternary aminocellulosic and quaternary chitosan derivatives in order to select those derivatives exhibiting desirable viscosifying power for use in comparative studies with Polyquaternium 10.

2.2 VISCOSITY

Viscosity is an expression of the resistance to flow of a system under an applied stress. The more viscous the liquid, the greater the applied force required to make it flow at a particular rate.⁶⁷ Viscosity is the proportionality constant between an applied force (per unit area) and the shear rate.

A liquid is sandwiched between two parallel plates and a shear force, F , is applied by the top surface of area, A (Figure 2.1). The force per unit area is $\sigma = F / A$. As a result, the upper surface, Δy , begins to move at a velocity, u .⁶⁸ The lower plate remains fixed. Within a liquid layer there will be a gradation of velocities. Liquid at the top plate will have a velocity equal to that plate while liquid near the bottom will be stationary. For "Newtonian fluids" the gradation of velocities is uniform, no matter how fast one plate is moved with respect to another.⁶⁸ This gradient of velocities is known as the shear rate, γ .

$$\gamma = du(y) / dy \quad (2.1)$$

Shear is the deviation from equilibrium position divided by the sample thickness

$$\gamma = \Delta x / \Delta y \quad (2.2)$$

The force applied by the upper plate will increase linearly with shear rate. Therefore, viscosity is defined as

$$\eta = \sigma / \dot{\gamma} \quad (2.3)$$

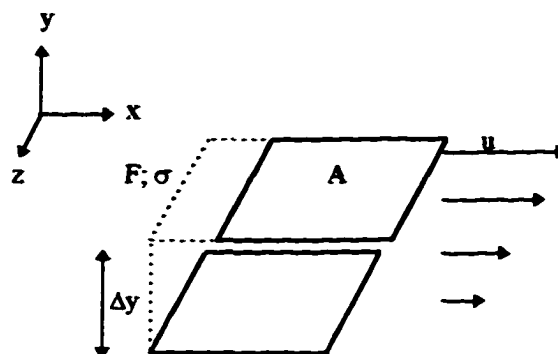


Figure 2.1: Shear Force Required to Produce a Velocity Gradient Between Parallel Layers of a Fluid.

There are three viscosity coefficients commonly determined to characterize polymer solutions: relative viscosity, η_{rel} , specific viscosity, η_{sp} , and intrinsic viscosity, $[\eta_{int}]$. The equations for the determination of these coefficients are given in Equations 2.4 - 2.6.

$$\eta_{rel} = (\eta_{solution} / \eta_{solvent}) \quad (2.4)$$

$$\eta_{sp} = (\eta_{solution} / \eta_{solvent}) - 1 \quad (2.5)$$

$$[\eta_{int}] = \lim_{c \rightarrow 0} (\eta_{rel} / c) = \lim_{c \rightarrow 0} (\eta_{sp} / c) \text{ extrapolated to } c = 0 \quad (2.6)$$

The viscosity of a fluid decreases with increasing temperature ^{67,68} and is related by an experimental equation:

$$\eta = A \exp (E_v / R T) \quad (2.7)$$

where A is a constant depending on the molecular weight and molar volume of the fluid and E_v is an activation energy required to initiate flow between the molecules.⁶⁷ More energy is required to break bonds and permit flow in fluids composed of molecules that form hydrogen bonds. ⁶⁷

2.3 FLOW

There are three types of non-Newtonian flow: plastic, pseudoplastic and dilatant (Figure 2.2). In plastic flow the curve does not pass through the origin, but intersects the shearing stress axis at a point called the yield value. The material does not begin to flow until the yield value has been exceeded. At stresses below this value, the material acts as an elastic material. Plastic flow is associated with flocculated particles in a suspension. Generally, pseudoplastic flow is exhibited by polymers in solution. There is no yield value in these systems. However, no part of the curve is linear; therefore, the viscosity can not be expressed by any single value. The viscosity of a pseudoplastic material decreases with increasing shear rate. As the shearing stress is increased, the molecules begin to align along their axis in the direction of flow and the internal resistance of the material is decreased. Dilatant flow is exhibited by systems that contain a high percentage of dispersed solids. The resistance to flow increases as the shear rate is increased and an increase in volume is observed. When the stress is removed, the system returns to its state of fluidity. ⁶⁷

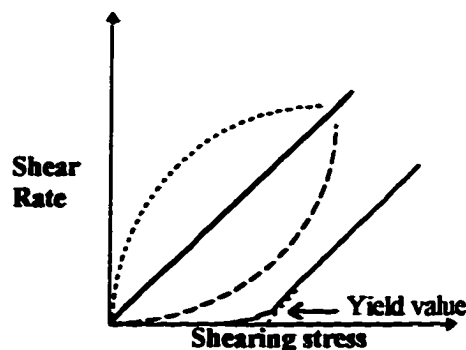


Figure 2.2: Three Types of non-Newtonian Flow:

- Newtonian
- Plastic
- - - - - Pseudoplastic
- Dilatant

2.4 VISCOSITY OF POLYELECTROLYTE SOLUTIONS

Polyelectrolytes are a class of macromolecules that spontaneously acquire a large number of elementary charges distributed along the backbone when dissolved in a suitable polar solvent, usually water.⁶⁹ There are two classes of polyelectrolytes: strong and weak. Strong polyelectrolytes spontaneously acquire full charge when dissolved in pure solvent. Weak polyelectrolytes are partially charged in pure solvent and can be titrated to full charge with either a strong acid or base. The distinction depends upon solvent, temperature, concentration, and other experimental conditions. When in solution and charged, each polyelectrolyte is accompanied by an equivalent amount of low molar mass (LMM) ions of opposite charge. These LMM ions are the counterions.

Polyelectrolyte solutions exhibit both chain like properties and properties due to electric charges. They are characterized by an increase in viscosity with respect to that of the pure solvent. In a given solvent, increases in viscosity at constant temperature

depend upon molar mass of the polyelectrolyte, concentration, linear charge density and concentration of LMM inert electrolyte (salt) added.^{68,69} When an excess of LMM salt is added, the viscosity of a polyelectrolyte solution behaves like that of a neutral macromolecule solution (Figure 2.3, curves E and F). However, the viscosity of solutions without added LMM salt deviates from this behavior (Figure 2.3, curves A through D). This deviation is due to the decrease in electrostatic screening of the charges on the polymer backbone as the screening arises only from the counterions.

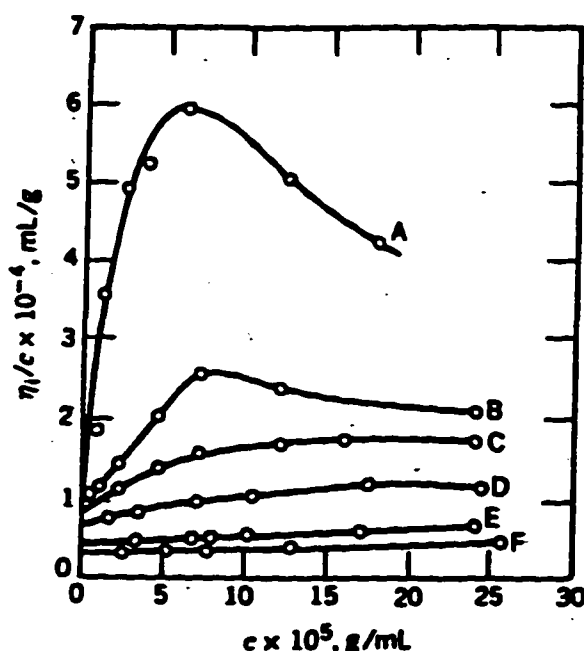


Figure 2.3: Reduced Viscosity Numbers of Aqueous Solutions of 60.8% Poly(vinylbutylpyridinium bromide) as a Function of Polymer and NaCl concentration. A = water; B - F, in $c_{\text{NaCl}} = 10^{-4}$ mol/L: B, ca 0.2; C, 10; D, 25; E, 60, F, 100 (Reproduced from Reference #1 in M. Mandel, Polyelectrolytes, In: Encyclopedia of Polymer Science and Engineering, Second edition, John Wiley & Sons, New York, 1988. Copyright © 1988, John Wiley & Sons, Inc., Reprinted by permission of John Wiley & Sons, Inc.).

At constant temperature, solvent, and added LMM salt, the viscosity increment of a polyelectrolyte in water usually increases with increasing linear charge density.⁶⁹ These viscosity curves may be extrapolated to zero concentration of polyelectrolyte in order to determine the intrinsic viscosity. However, viscosity data for solutions without added LMM salt are more difficult to interpret. At constant temperature and linear charge density, the reduced viscosity exhibits a non-linear concentration dependence which impedes the determination of the intrinsic viscosity (Figure 2.3, curve A).⁶⁹ Extrapolation to zero concentration gives values of the intrinsic viscosity that are either too low or negative.

2.5 EXPERIMENTAL

The viscosity and c^* values for the quaternary aminoalkylcarbamoyl cellulosic and chitosan derivatives were determined in doubly distilled water by means of a Cannon - Ubbelohde four-bulb viscometer at 26 ± 0.2 °C and a Wells - Brookfield cone and plate viscometer at 20 ± 0.1 °C, respectively. Brookfield viscosity was measured using an ASTM method.⁷⁰ All the polymers were dialysed prior to use against distilled, deionized water in a cellulose acetate dialysis tube with a 6-8,000 Dalton cutoff to remove low molar mass electrolyte. Viscosity measurements were made without addition of LMM electrolyte.

2.6 RESULTS AND DISCUSSION

The reduced viscosity, η_{sp} / c , of aqueous solutions of the quaternary aminoalkylcarbamoyl cellulose and chitosan derivatives was determined without added electrolyte using an Ubbelohde viscometer. The objective of this study was to determine the three major concentration regions (dilute, semi-dilute and concentrated) as the

polymer properties and nature of surfactant interaction vary in each region. Huggins plots of η_{sp} / c versus polymer concentration (Figures 2.4 and 2.5) indicate that the specific viscosity decreases with decreasing polymer concentration until a plateau region is entered where the change in viscosity with concentration is small. In the case of DQNNED, this plateau region is not as pronounced as the viscosity of the solution is high. As the concentration is further decreased, the viscosity begins to increase and reach a second maximum. Further dilution causes the viscosity to decrease as the polymer concentration approaches zero.

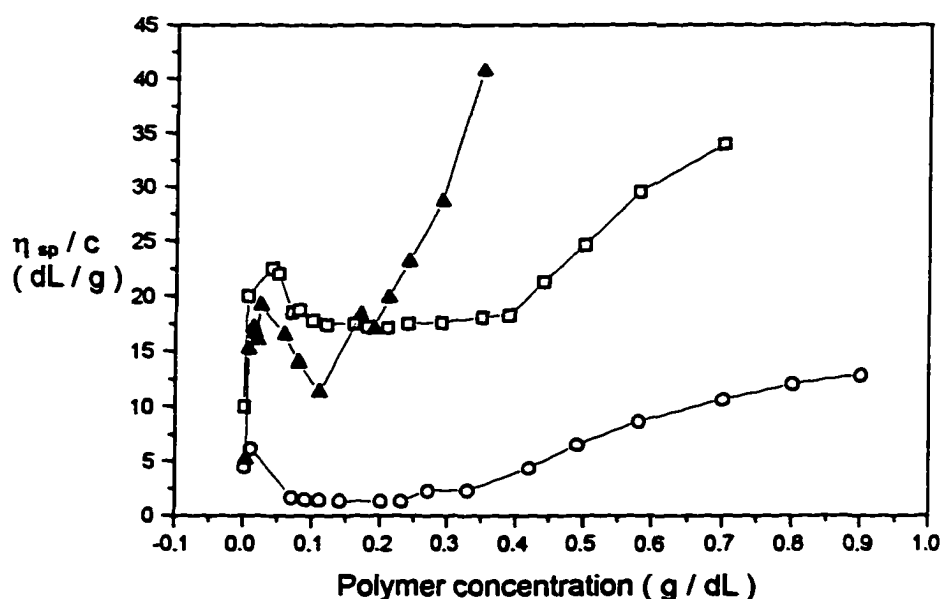


Figure 2.4: Ubbelohde Viscosity of Quaternary Polymers: \square Polyquaternium 10; \circ MQNNED; and \blacktriangle DQNNED

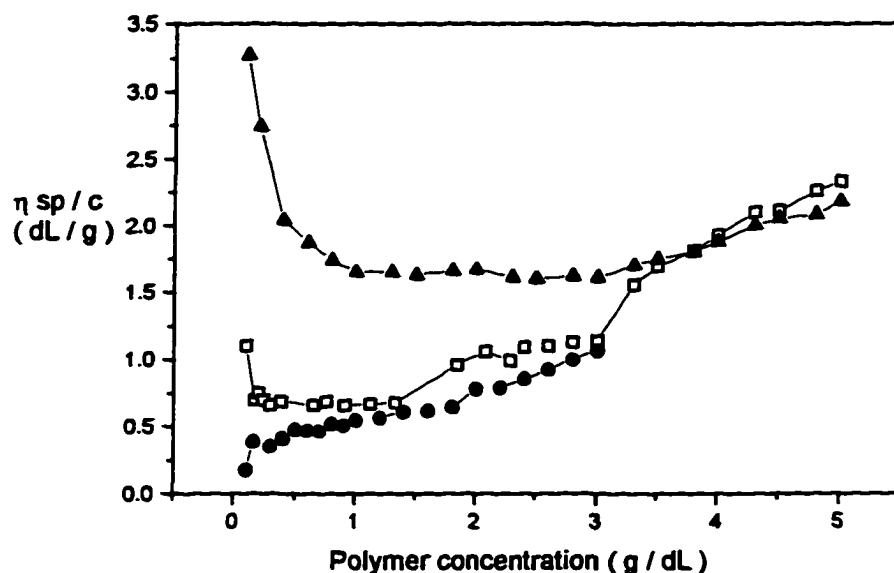


Figure 2.5: Ubbelohde Viscosity of Quaternary Polymers: □ PQNNED; ● CMCJ600; and ▲ CHI-Q188

This behavior is known as the polyelectrolyte effect. Early studies of semidilute and moderately semidilute “salt free” polyelectrolyte solutions⁷¹ resulted in the following empirical relationship between η_{sp} / c and the concentration of polymer, c :

$$\eta_{sp} / c = A / (1 + B c^{1/2}) \quad (2.8)$$

This equation (2.8), known as the Fuoss law, yields a straight line when η_{sp} / c is plotted *versus* $c^{1/2}$. It was assumed that this line could be extrapolated to zero concentration and that the intercept gives the value of $[\eta_{int}]$. The large values of $[\eta_{int}]$ obtained from these plots were thought to indicate that the polyelectrolytes become fully stretched in the dilute regime.⁷² The cause of this behavior was believed to be the loss of counterion shielding at low ionic strength (Figure 2.6). The charges on the polymer chain are confined to the chain itself while the counterions are not confined. Therefore, at high

concentration, intramolecular charge-charge repulsions can be screened by the less rarefied ionic atmosphere. This effect was thought to produce regions of high charge density, charge - charge repulsion, chain extension and increased viscosifying power.

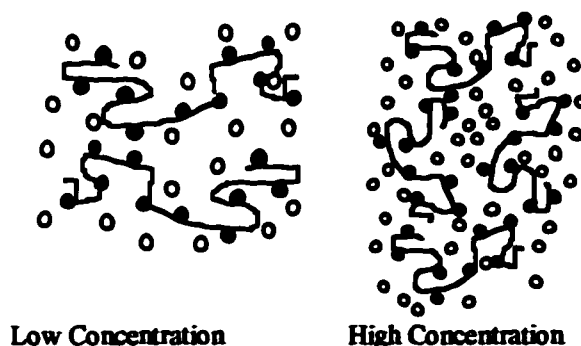


Figure 2.6: The Polyelectrolyte Effect: ● Cationic charged moiety; ○ Anionic Counterion

Recently, Cohen *et al.* ⁷³ have shown that linear extrapolation to zero concentration is incorrect. These authors show that at very low polyelectrolyte concentration ($< 10^{-5}$ g/ml) the reduced viscosity decreases with decreasing concentration. This result is similar to studies of isoionic dilution of polyelectrolytes. ^{74,75} Recently, an alternative expression for the dilute solution viscosity has been proposed. ⁷⁶ Rabin *et al.* have used a modified version of theory originally proposed by Hess and Klein for suspensions of highly charged, spherical particles. ⁷³ They show that the change in the viscosity is related to the nature of the strong electrostatic repulsions between the polyelectrolytes. ⁷⁶ Using an extremely accurate and precise viscometer system, Cohen *et al.* ⁷³ have measured the viscosity of dilute solutions ($< 10^{-5}$ g/ml) of sodium poly(styrene sulfonate). Their results show that increasing the molecular weight produces an increase in the viscosity observed in the dilute regime. However, the

concentration at which the maximum viscosity occurs is independent of molecular weight. No qualitative change of behavior was observed as the polymer concentration was increased above the overlap concentration, c^* . The positions and heights of the maxima were dependent on LMM salt concentration; increases in LMM salt moved the maxima to higher polymer concentration and decreased the reduced viscosity. The reduced specific viscosity at the maxima was found to increase linearly with molecular weight of the polyelectrolyte. The slopes and intercepts of the lines were found to decrease with increasing LMM salt. These results prompted the authors to suggest a generalized Fuoss formula (Eq. 2.9) that should replace the original Fuoss law (Eq. 2.8):

$$\eta_{sp} \approx (R_H l_B^2 c_p) / \kappa^3 \quad (2.9)$$

where R_H is the hydrodynamic radius of the polyelectrolyte which is proportional to its molecular weight for a fully stretched chain, $l_B = e^2 / \epsilon_0 k_B T$ is the Bjerrum length, and κ^{-1} is the Debye screening length.⁷⁶ The dominant contribution to the viscosity comes from wave vectors of order κ for which the direct correlation function becomes small because of exclusion effects (i.e. strong electrostatic repulsion between polyelectrolytes). The authors hypothesize that, independent of polyelectrolyte concentration, the behavior of LMM salt polyelectrolyte solutions is in many respects similar to that of a dense fluid of hard spheres with effective hardcore radii κ^{-1} .⁷³ In light of these results and comparison of our viscometer system with that of Cohen *et al.*⁷³, we are unable to explain the increases in reduced viscosity upon dilution as we are most probably not truly in the dilute regime ($< 10^{-5}$ g/ml). The phenomena observed in Figure 2.4 and 2.5 may result from either the adsorption of the polyelectrolyte on the glass surface of the

Ubbelohde viscometer, the polyelectrolyte effect, or polydispersity. We will therefore concentrate on the critical overlap concentration of these polymers.

All six polymers studied show different viscosities at similar concentrations regardless of number of cationic charges per graft or graft rigidity. Polyquaternium 10, MQNNED and DQNNED have viscosities significantly greater than the other polymers. PQNNED, CMCJ600 and CHI-Q188 exhibit viscosities much lower than either Polyquaternium 10, MQNNED or DQNNED. The critical overlap concentration, c^* , is the concentration at which the polymer chains just begin to overlap with each other. The value of c^* is defined as the concentration at which the product of the concentration and the intrinsic viscosity is equal to unity (Eq. 2.10).⁷⁷ However, in this work, the overlap concentration is determined as the concentration at which an abrupt change in slope occurs in the Huggins plot (η_{sp}/c versus c) (Eq. 2.11). The choice of the break point in the curve is justified by scaling arguments.^{69,78,79} Theoretically, the specific viscosity should scale as the 1.4th power of the product of the concentration and intrinsic viscosity at concentrations below c^* (Eq. 2.12).⁷⁷ At concentrations above c^* , the scaling factor should be 3.3 (Eq. 2.13).⁷⁷

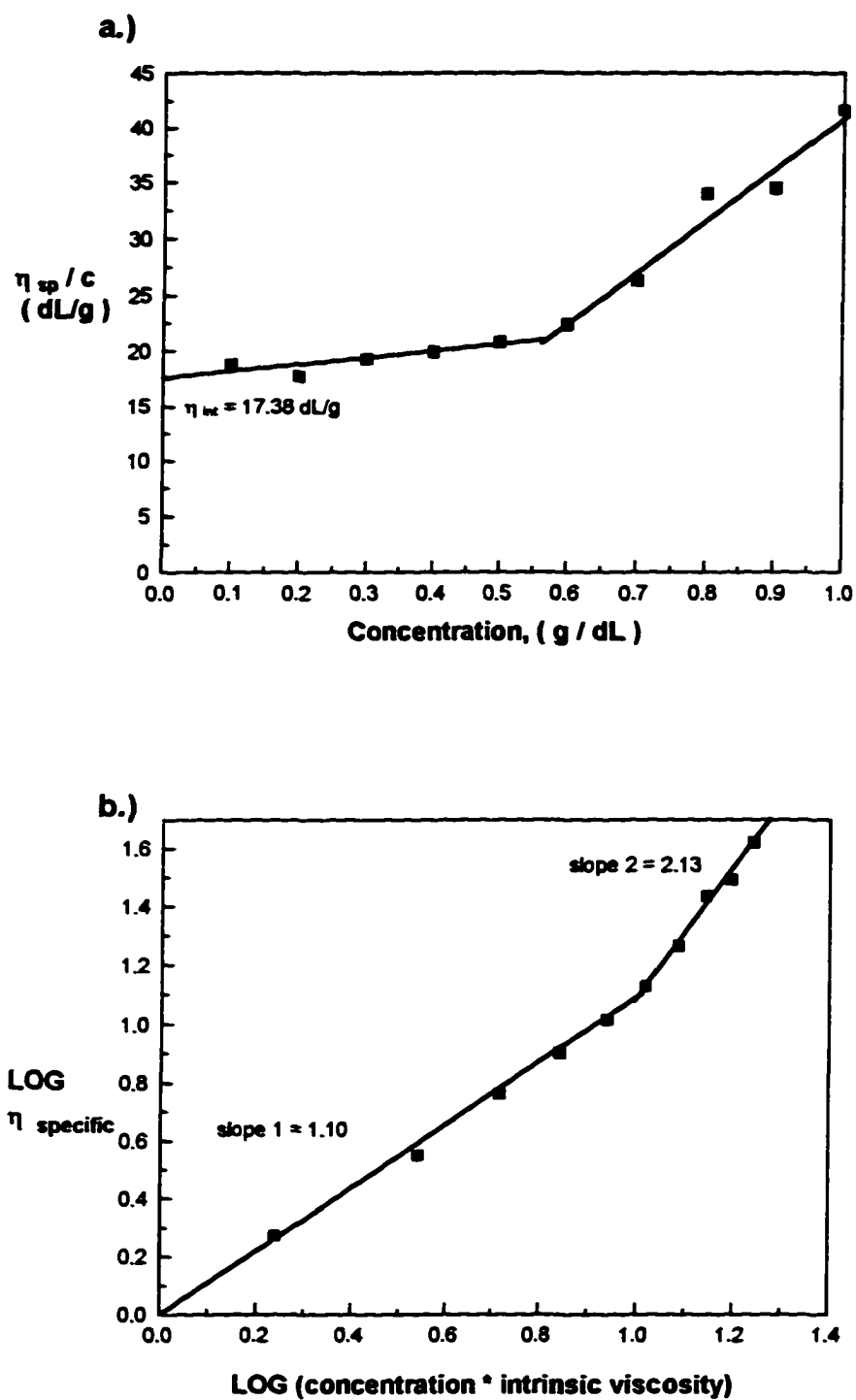
$$[\eta]_{int} c = 1 \quad (2.10)$$

$$\eta_{sp}/c = [\eta]_{int} + k'_1 [\eta]_{int}^2 c + k''_1 [\eta]_{int}^3 c^2 + \dots + \quad (2.11)$$

$$\eta_{solution} = \eta_{solvent} (1 + (c [\eta]_{int})^{1.4}) \quad (2.12)$$

$$\eta_{solution} = \eta_{solvent} (1 + (c [\eta]_{int})^{3.3}) \quad (2.13)$$

Using a Wells - Brookfield cone and plate viscometer, the apparent critical overlap concentrations, c^*_{app} , were determined for the quaternary polymers from Huggins and modified Huggins plots (Figures 2.7 - 2.12). We have chosen to designate



**Figure 2.7: Huggins and Modified Huggins Plots for Polyquaternium 10:
a.) Huggins Plot and b.) Modified Huggins Plot.**

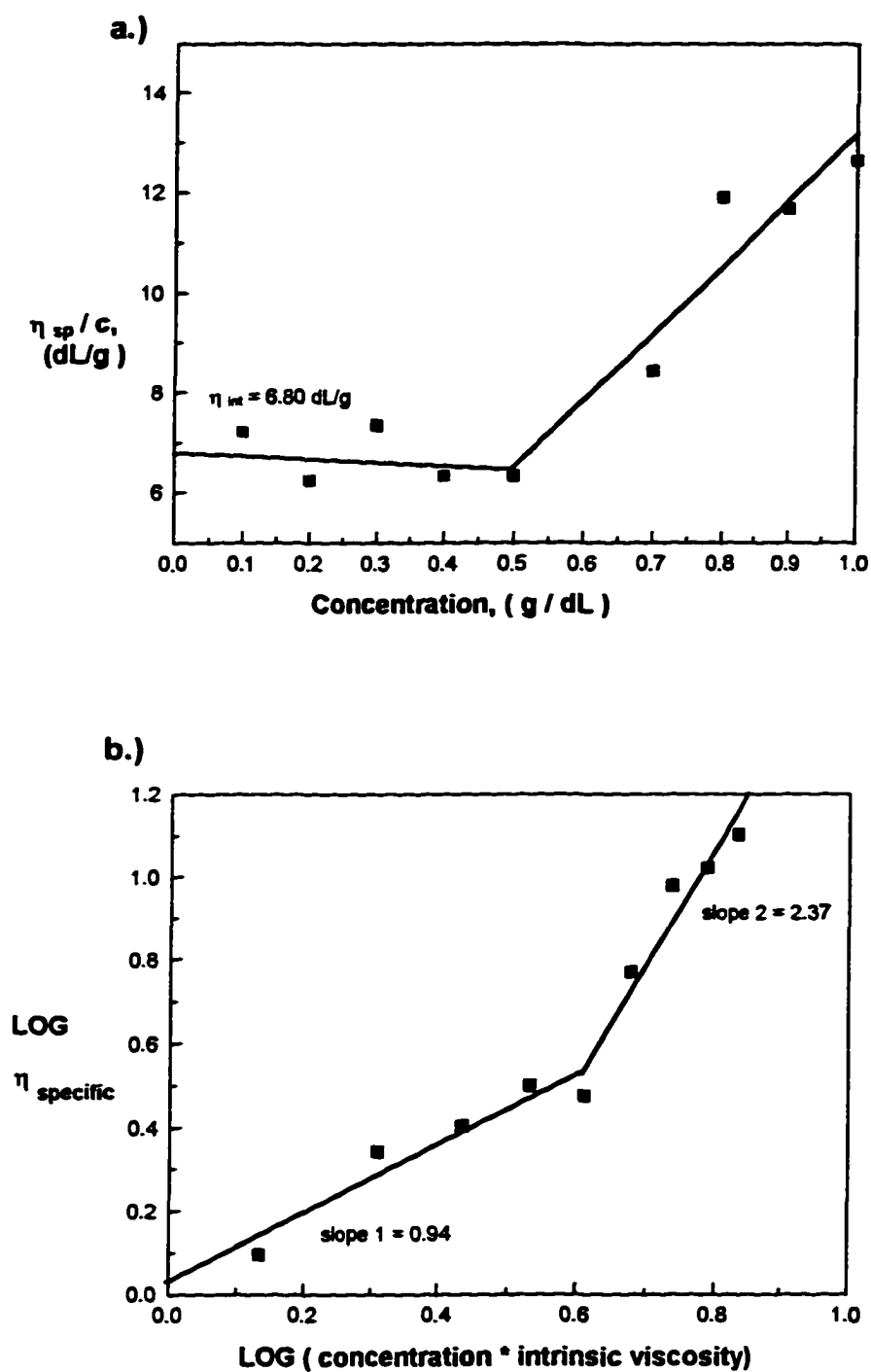


Figure 2.8: Huggins and Modified Huggins Plots for MQNED: a.) Huggins Plot and b.) Modified Huggins Plot.

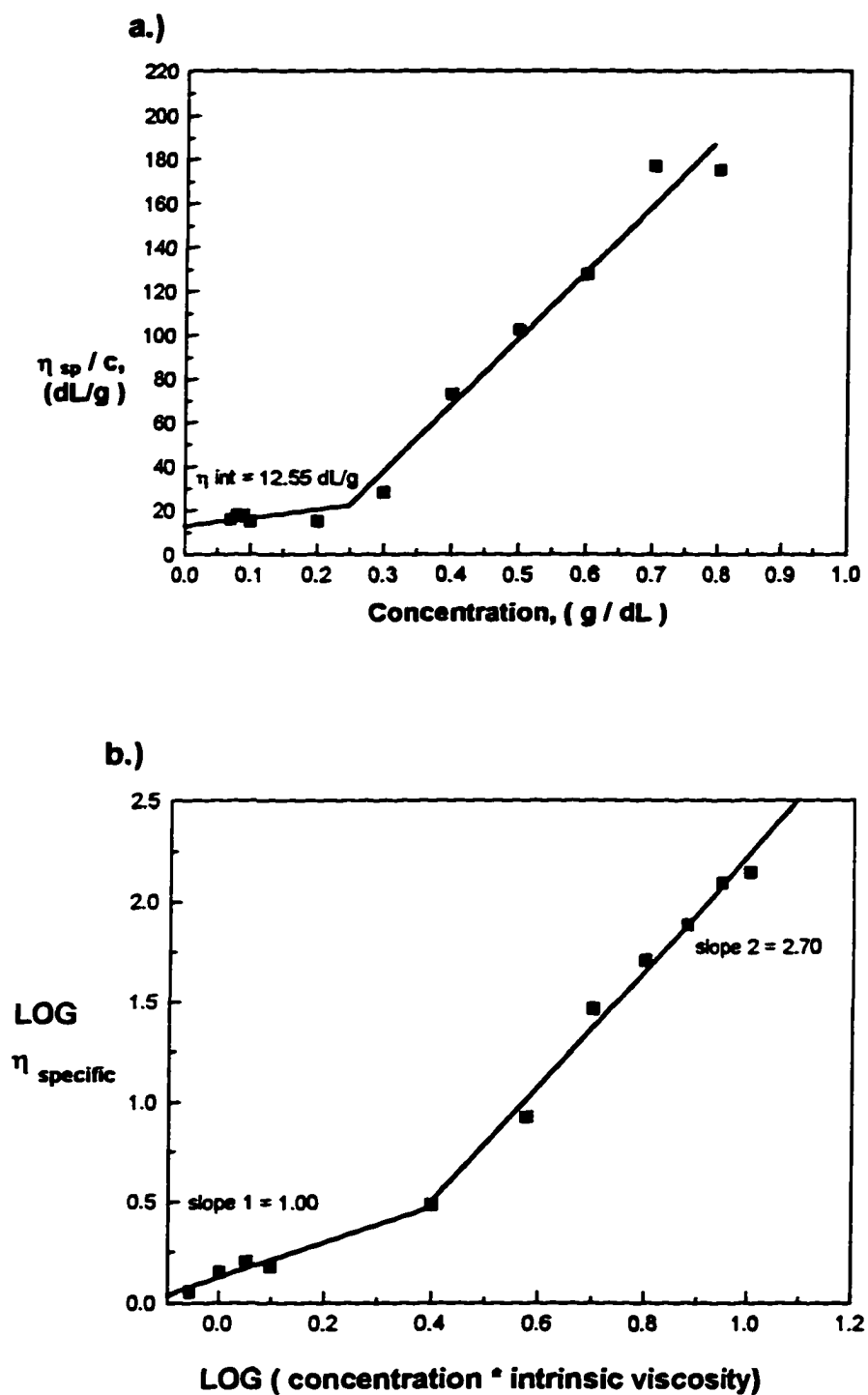


Figure 2.9: Huggins and Modified Huggins Plots for DQNNED: a.) Huggins Plot and b.) Modified Huggins Plot.

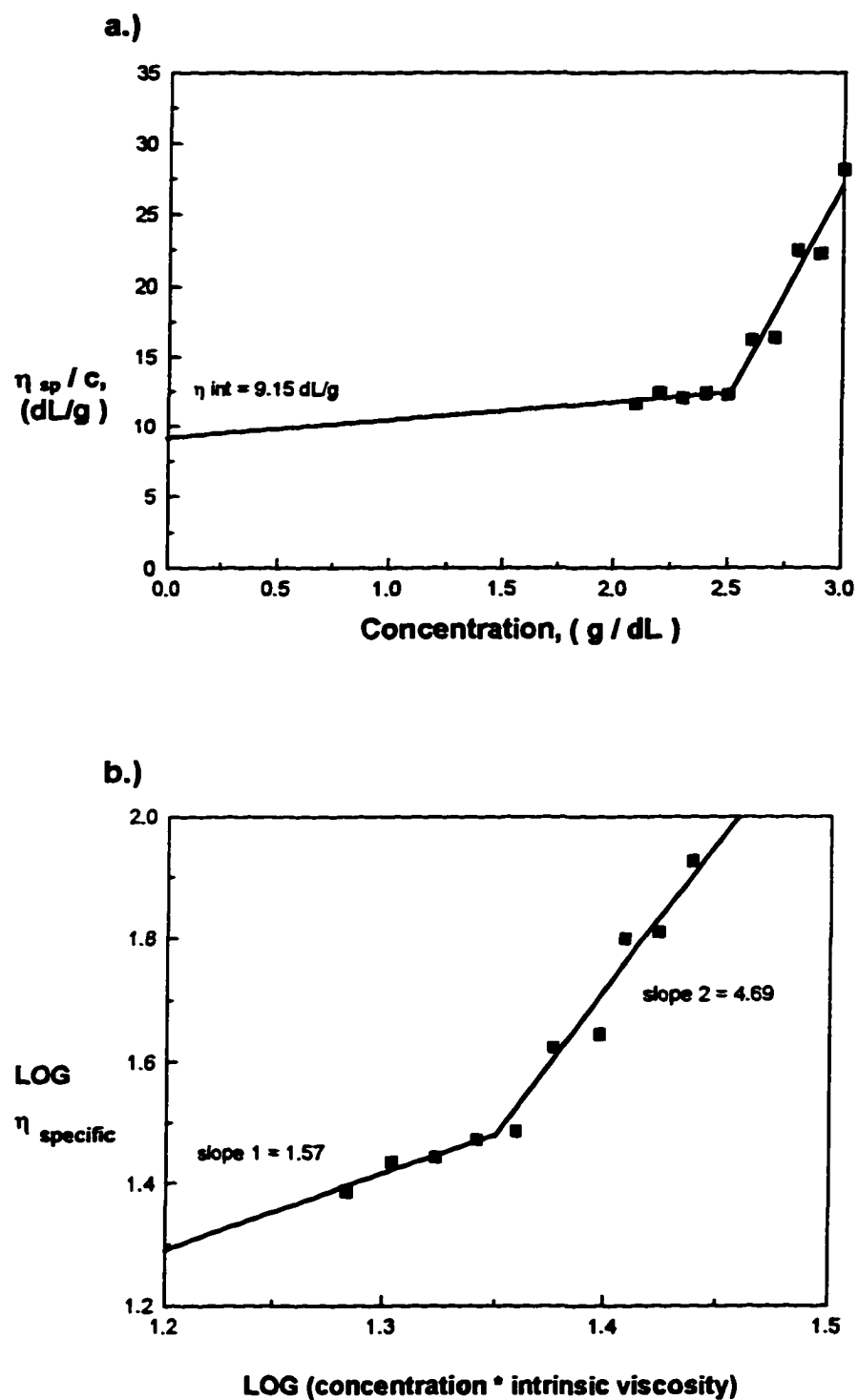


Figure 2.10: Huggins and Modified Huggins Plots for PQNED: a.) Huggins Plot and b.) Modified Huggins Plot.

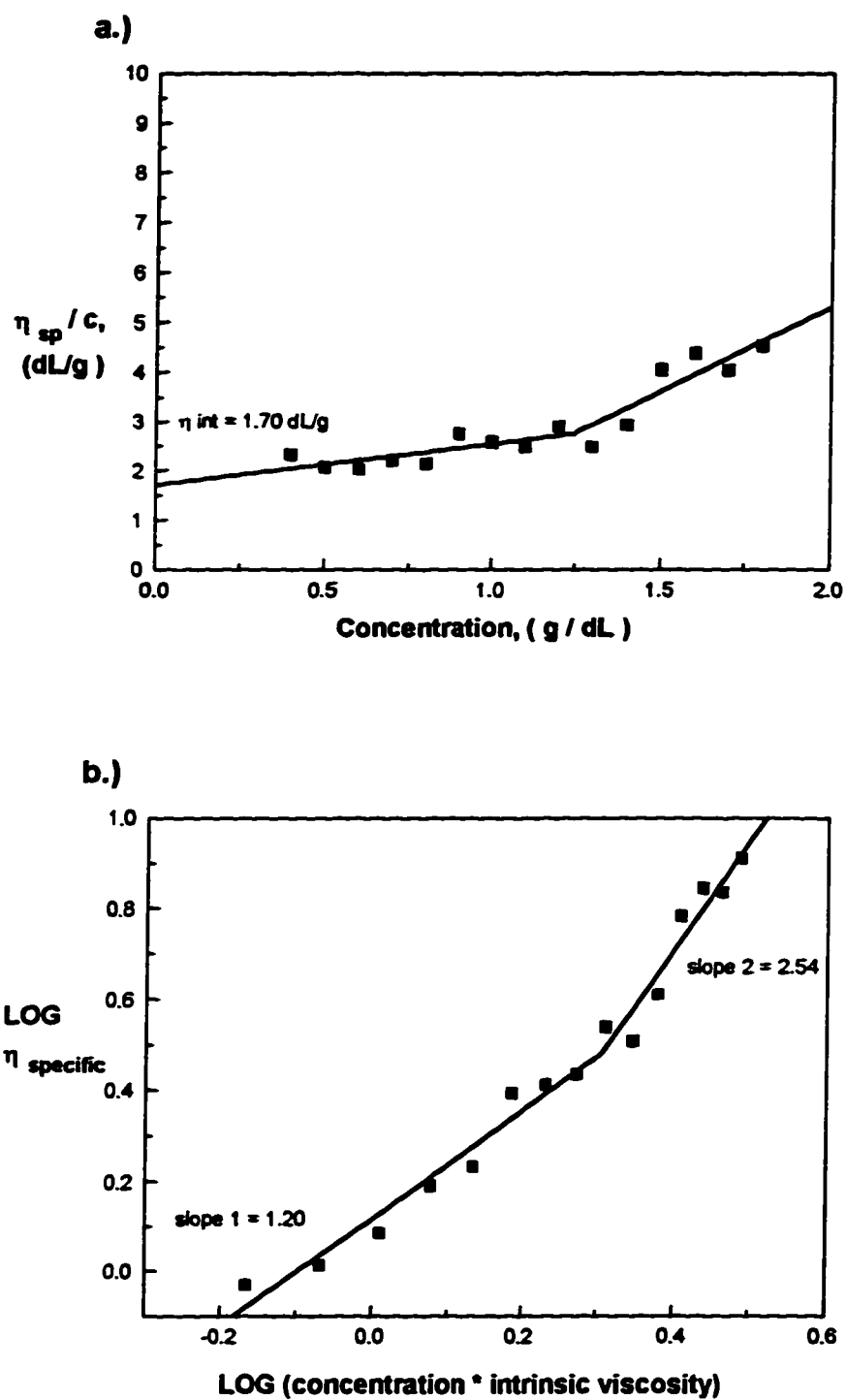


Figure 2.11: Huggins and modified Huggins Plots for CMCJ600: a.) Huggins plot and b.) modified Huggins plot.

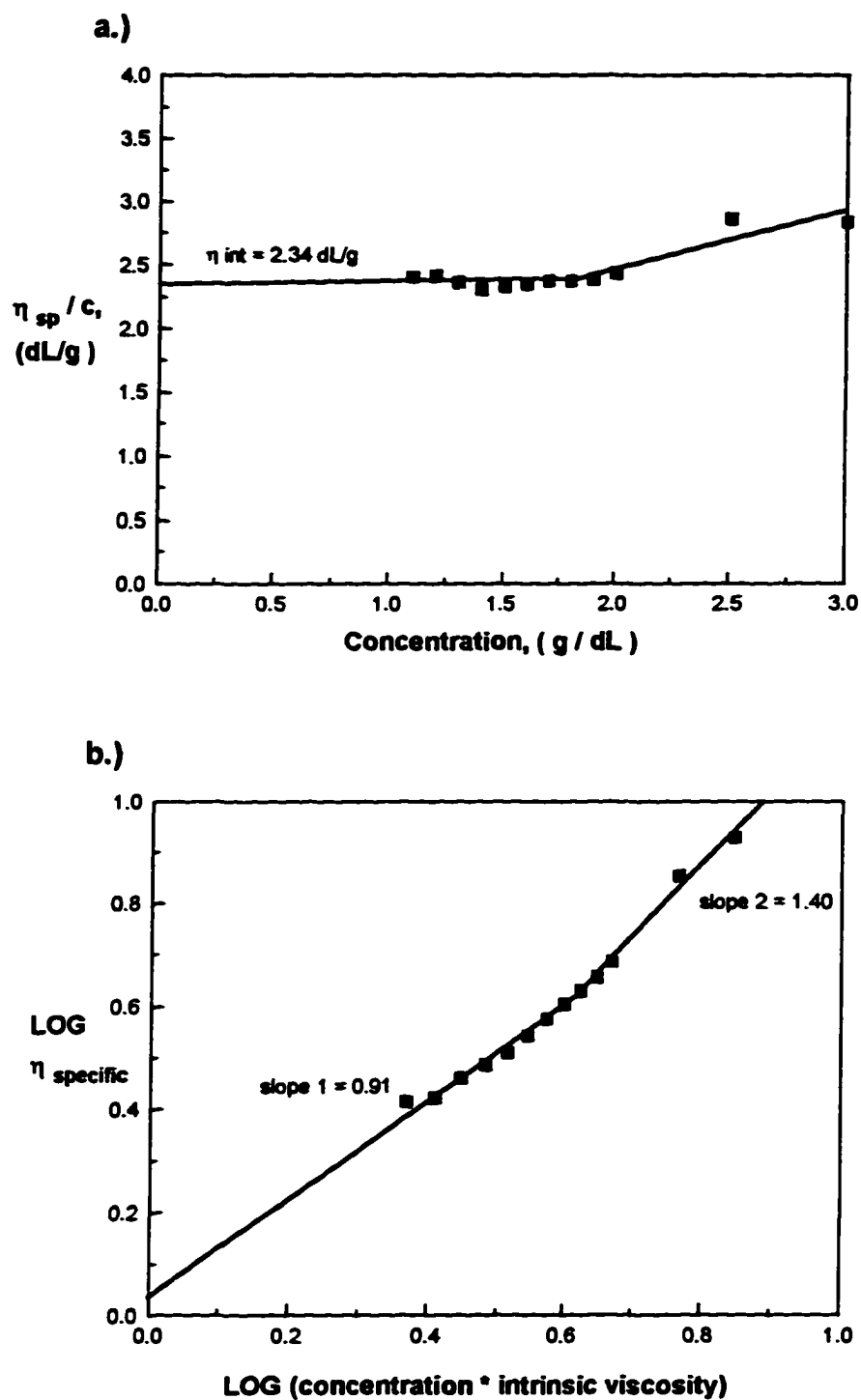


Figure 2.12: Huggins and Modified Huggins Plots for CHI-Q188: a.) Huggins Plot and b.) Modified Huggins Plot.

these values as c^*_{app} as extrapolation to zero concentration for a polyelectrolyte without added electrolyte is reported to yield values of $[\eta]_{int}$ which are either too low or negative.^{69,75}

The values of c^*_{app} , the overlap parameter, the scaling exponents, and $[\eta]_{int,app}$ for the quaternary cellulose and chitosan derivatives are given in Table 2.1. DQNNED which contains two cationic charges per graft exhibited the highest reduced specific viscosity, approximately 185 dL/g, and the lowest value of c^*_{app} . Both monoquaternary polymers, Polyquaternium 10 and MQNNED, exhibited similar values of c^*_{app} despite their differences in graft rigidity and reduced viscosity number. Significantly higher values for c^*_{app} were found for the remaining polymers. In the case of PQNNED which contains approximately five cationic charges per graft and CMCJ600 which has a quaternary nitrogen at the end of a long flexible graft, the high values of c^*_{app} and low viscosities may be attributed to aggregation. The high value of c^*_{app} determined for CHI-Q188 may be attributed to the significantly lower molecular weight of the chitosan derivative compared to the cellulose derivatives. The cellulose derivatives have a starting molecular weight of 250,000 g/mol prior to modification whereas the chitosan derivative has a starting molecular weight of 100,000 g/mol. Comparison of the scaling exponents determined from the modified Huggins plots with the reported scaling exponents of 1.4 and 3.3⁷⁷ indicates that the choice of the breakpoint for c^*_{app} appears to be reasonable.

The coil overlap parameter, $[\eta]_{int,app} c^*_{app}$, indicates the degree of overlap among polymer molecules. The degree of overlap effects the concentration and molecular weight dependence of viscosity. The overlap parameter for Polyquaternium

Table 2.1: Values of c^*_{app} , the Overlap Parameter, the Scaling Exponents, and $[\eta_{int}]_{app}$ from Huggins and Modified Huggins Plots

| Polymer | $[\eta_{int}]_{app}$ (dL / g) | c^*_{app} (g / dL) | Overlap parameter $[\eta_{int}]_{app} c^*_{app}$ | 1 st Scaling Exponent | R for 1 st Scaling Exponent | 2 nd Scaling Exponent | R for 2 nd Scaling Exponent |
|----------------------|----------------------------------|-------------------------|--|-------------------------------------|--|-------------------------------------|--|
| Polyquaternium 10 | 17.39 | 0.57 | 9.91 | 1.10 ± 0.03 | 0.99769 | 2.13 ± 0.07 | 0.99445 |
| MQNNED | 6.80 | 0.50 | 3.40 | 0.94 ± 0.09 | 0.95168 | 2.37 ± 0.30 | 0.96486 |
| DQNNED | 12.55 | 0.25 | 3.14 | 1.00 ± 0.18 | 0.97300 | 2.69 ± 0.22 | 0.98080 |
| PQNNED | 9.15 | 2.50 | 22.8 | 1.57 ± 0.37 | 0.97500 | 4.70 ± 0.30 | 0.97361 |
| CMCJ600 | 1.70 | 1.25 | 2.12 | 1.20 ± 0.02 | 0.97738 | 2.54 ± 0.20 | 0.95142 |
| CHI-Q188 | 2.34 | 1.75 | 4.10 | 0.91 ± 0.02 | 0.99191 | 1.40 ± 0.01 | 0.98784 |

10 is greater than that of either MQNNED or DQNNED. This result may be attributed to the numerous sites for hydrogen bonding between molecules of Polyquaternium 10 compared with hydrogen bonding of either MQNNED or DQNNED. Increased hydrogen bonding between polymer molecules increases the number of contact points between the polyelectrolyte chains and results in a higher viscosity.

2.7 CONCLUSIONS

Comparison of the quaternary aminoalkylcarbamoyl cellulosic and chitosan derivatives by viscosity indicates that the derivatives containing a low number of cationic charges per graft and shorter graft length have the highest viscosifying power. Therefore, the two polymers, PQNNED and CMCJ600, will be omitted from further studies as they do not exhibit properties desirable for use in cosmetic formulation, particularly as rheology modifiers.

CHAPTER 3: VISCOSITY WITH ETHANOL

3.1 INTRODUCTION

Naturally occurring polymers such as tragacanth, arabic or karaya gum were used in early hair fixative products.⁸⁰ These fixatives were delivered from either aqueous or hydroalcoholic media to damp hair. The hair was then styled and allowed to dry on rollers. This type of product was insufficient for all hairstyles and, as a result, an improved, quick drying product known as hair spray was developed.

Shellac was the first polymer to be used in hair sprays.^{80,81} Unfortunately, both the consumer and the formulator encountered difficulties with this polymer and synthetic resins were developed. Presently, the continued effort to synthesize new polymeric resins has been driven by consumer demand for fixative products that demonstrate both humidity resistance and ease of removal by shampooing.⁸²

Since the banning of chlorofluorocarbons (CFC's) in 1979, other regulatory acts have followed.⁸⁰⁻⁸⁴ Today, the most pressing issue is the reduction in the amount of volatile organic compounds (VOC's) allowable in cosmetic formulations. The most obvious solution is the substitution of water for the amount of alcohol or propellant that must be removed.⁸⁰⁻⁸³ This will result in the same challenge that was presented to formulators over fifty years ago: how to create a quick drying fixative product which demonstrates both humidity resistance and ease of removal in an aqueous or low level hydroalcoholic solution. Replacement of the volatile solvents will require fabrication of products with selective affinity for hair.

Since many cosmetic formulations contain ethanol as a drying agent, it would be interesting to determine the solubility of the quaternary aminoalkylcarbamoyl cellulose and chitosan derivatives in aqueous - alcoholic solutions, the clarity of the solutions and

viscosity. The results will be compared with Polyquaternium 10 which is soluble in aqueous - alcoholic solutions up to 50% alcohol and is used in personal care products.

3.2 EXPERIMENTAL

The viscosity of 1% solutions of the aminoalkylcarbamoyl cellulose and chitosan derivatives was determined in ratios of doubly distilled water and ethanol by means of a Wells - Brookfield cone and plate viscometer at 20 and 40 ± 0.1 °C. The solutions were filtered and the filtrates were optically clear.

All the polymers studied were soluble in ratios of water and ethanol up to approximately 60% ethanol. In the case of CHI-Q188, solubility was observed up to 100% ethanol. The three other polymers tended to swell in solutions containing ethanol in excess of 60%.

3.3 RESULTS AND DISCUSSION

The “viscosifying power”, η_{sp} / c , of 1% solutions of the quaternary aminoalkylcarbamoyl cellulose and chitosan derivatives was determined with various amounts of ethanol and water (Figure 3.1). Interestingly, there appears to be an increase in viscosity of the solution containing only water and ethanol around 55-60% ethanol. This effect is also observed in the solutions containing Polyquaternium 10, MQNNED and CHI-Q188 and is attributed to the ordering of the water molecules solvating the polymers by ethanol.

In general, the addition of ethanol decreases the viscosity of the solutions. However, the viscosity of the DQNNED solution was unaffected by the addition of ethanol. A decrease in the viscosity may be detrimental to formulation of certain cosmetic products when a high viscosity is desired such as with gels. Therefore,

DQNNED appears to be a potential improvement over Polyquaternium 10 and the other monoquaternary polymers as its viscosity is unaffected by addition of ethanol. This may allow for lower concentrations of both polymer and ethanol to be utilized in formulation.

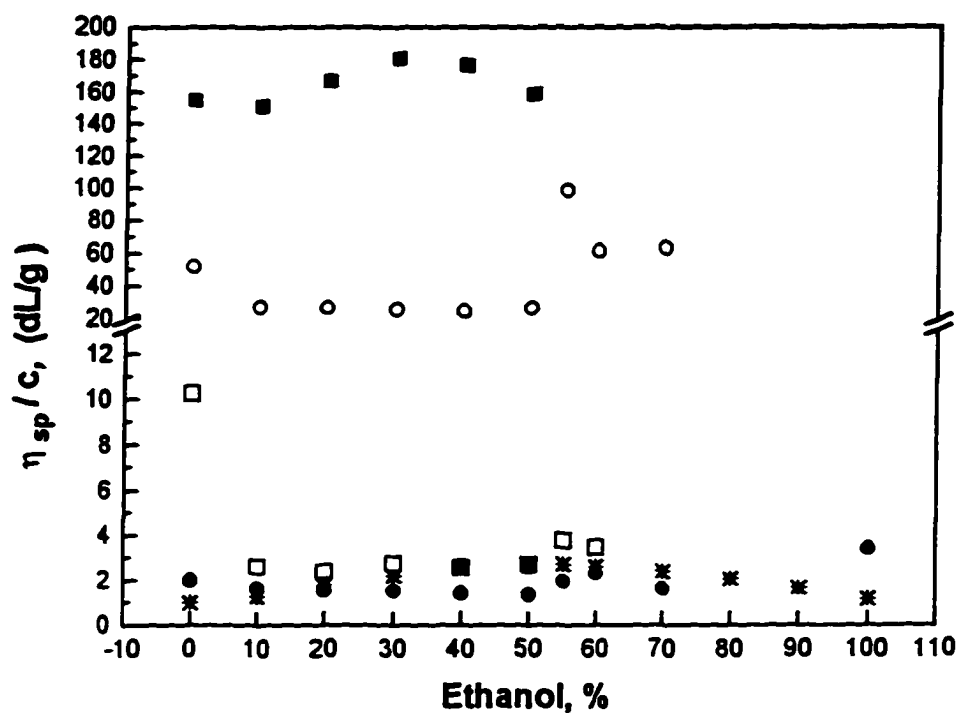


Figure 3.1: Dependence of η_{sp}/c on Percentage of Ethanol at 20 °C
 ○ Polyquaternium 10; □ MQNNED; ■ DQNNED; ● CHI-Q188; and
 * water and ethanol alone; $n =$ three measurements, the error bars are
 smaller than the data points

The viscosity of polymer solutions depends on temperature,⁶⁸; therefore, the temperature was increased to 40 °C in order to determine changes in viscosity of the solutions (Figure 3.2). As anticipated, the viscosity of the solutions has decreased with

increasing temperature. However, the slight increase in viscosity due to the water - ethanol ordering effect is still observed for the solutions of Polyquaternium 10 and MQNNED. The decrease in viscosity is not as significant for those solutions containing ethanol as a co-solvent when compared to water alone. The solution viscosity of DQNNED is greatly affected by the increase in temperature. This effect may be a result of loss of ethanol at 40 °C.

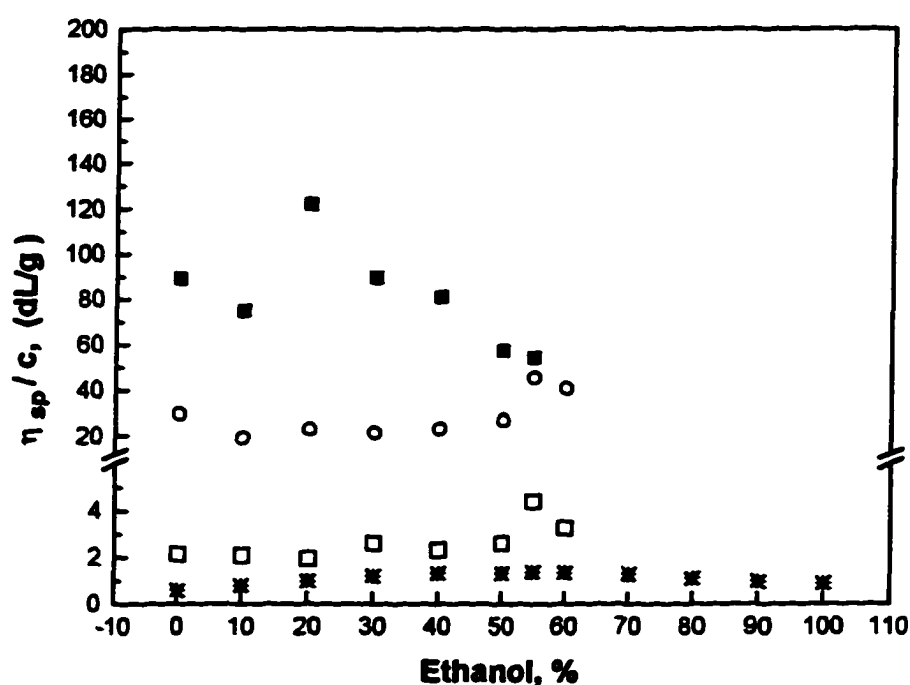


Figure 3.2: Dependence of η_{sp}/c on Percentage of Ethanol at 40 °C:
 ○ Polyquaternium 10; □ MQNNED; ■ DQNNED and * water and ethanol alone; $n = 3$ measurements, the error bars are smaller than the data points

3.4 CONCLUSIONS

Comparison of the quaternary aminoalkylcarbamoyl cellulosic and chitosan derivatives by viscosity with added ethanol indicates that DQNNED appears to be a potential improvement over Polyquaternium 10 and the other monoquaternary polymers as its viscosity is unaffected by addition of ethanol. This effect may allow for lower concentrations of both polymer and ethanol to be utilized in cosmetic formulation. Due to the low viscosity at all ratios of water and ethanol, CHI-Q188 will be omitted from further studies as it does not appear to exhibit properties desirable for use in cosmetic formulation, particularly as rheology modifiers.

CHAPTER 4:
PRECIPITATION STUDIES WITH SODIUM DODECYL SULFATE

4.1 INTRODUCTION

Polymer and surfactant interactions have been a subject of intense research⁸⁵⁻⁸⁸ resulting from the many industrial applications which make use of a polymer-surfactant system. Some of these industrial applications include cosmetic formulation,^{51-53,61,89,90} rheology control⁹¹ and drug release.⁹² Fundamentally, these systems are of interest as models for polyion-colloid systems, reversible equilibrium aggregates and natural supramolecular assemblies.

4.2 SURFACTANTS

Surfactants or surface active agents are molecules and ions that are adsorbed at interfaces.^{67,81} These molecules are amphiphilic meaning that the molecule has an affinity for both polar and nonpolar solvents (Figure 4.1). Depending on the nature of the surfactant, i.e. the number of polar and nonpolar groups present, the molecule may be predominantly hydrophilic (water loving), hydrophobic (oil loving) or well balanced between the two extremes. This amphiphilic nature of the surfactant molecules

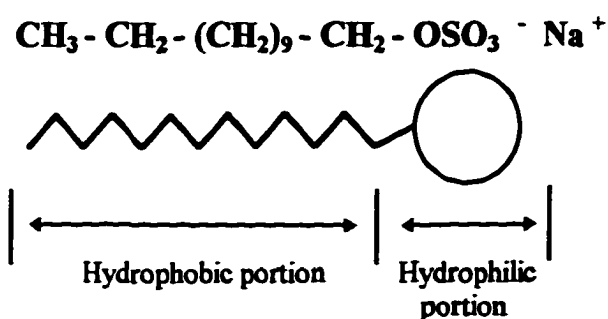


Figure 4.1: Structure of Sodium Dodecyl Sulfate.

(monomers) causes them to be adsorbed at the interface in this case the air water interface. Surfactant molecules may be anionic, cationic, nonionic or ampholytic (zwitterionic). Surfactants tend to minimize the contact of the hydrophobic groups with water. This minimization of contact is accomplished by adsorption at interfaces and association in solution.⁹³

Surfactant molecules, such as sodium dodecyl sulfate (SDS), when added to water orient themselves with the hydrophilic head group in the water and the hydrophobic tail in the air (Figure 4.2). A consequence of this orientation is that some of the water molecules at the interface will be replaced by hydrocarbon or other nonpolar groups. Since the interaction force between water molecules and nonpolar groups is less than that between water molecules and air molecules, adsorption of surfactants at the interface results in a reduction in the surface tension of the solution. The efficacy of the surfactant varies with the nature of the solvent, temperature, electrolyte concentration, and amount of impurities or additives in the system.⁹⁴

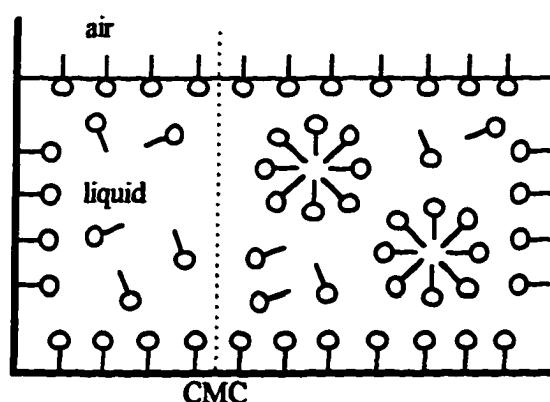


Figure 4.2: Orientation of Surfactant Monomers in Water.

When present in a liquid at low concentration, the surfactant monomers exist as solvated individual molecules. However, as the concentration is increased, aggregation occurs and micelles are formed. The concentration at which micelles are formed is termed the critical micelle concentration (CMC). Below the CMC the concentration of surfactant undergoing adsorption at the air water interface increases as the surfactant concentration is increased. When the interface and bulk phase become saturated the CMC is reached. Any further addition of surfactant creates different micellar structures in the solution and the free energy of the system is reduced. Micellization affects the physical properties of the solution including detergency, density, conductivity, surface tension, osmotic pressure, viscosity and interfacial tension (Figure 4.3). Surface tension is used as an indicator of the onset of micellization.

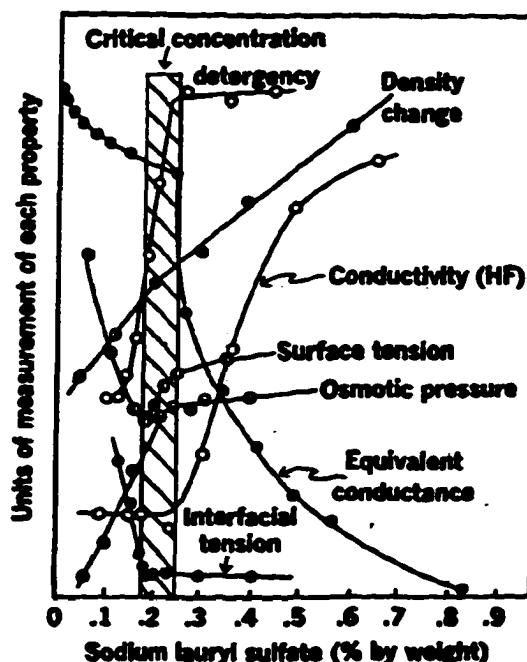


Figure 4.3: Changes in Physical Properties of Surfactant Solutions around the Critical Micelle Concentration. (With permission. Martin A. *et al.*, Physical Pharmacy, Third edition, Lea & Febiger, Philadelphia, 1983)

4.3 POLYMER - SURFACTANT INTERACTION

The interactions between polyelectrolyte and surfactant are largely dominated by electrostatic forces with hydrophobic interactions playing a secondary role in complex formation.⁸⁵⁻⁸⁸ Complexation of polyelectrolytes and oppositely charged surfactants begins at a surfactant concentration which is much lower than the critical micelle concentration (CMC) for the free surfactant.⁸⁸ This surfactant concentration which first results in complexation is known as the critical aggregation concentration (CAC).⁹⁵ In particular, for the case of a cationic polymer and anionic surfactant, it has been shown that the polymer-surfactant complex can not co-exist with free micelles if precipitation of the charge neutralized complex is observed.^{52,53,90} The region of maximum precipitation for the complex occurs near a stoichiometric charge neutralization (i.e. when the polymer-surfactant charge ratio is approximately 1:1).^{52,53,90} Addition of excess amount of anionic surfactant results in the resolubilization of the precipitated complex.^{52,53,90}

The interaction between cationic hydroxyethyl cellulose derivatives and oppositely charged surfactants has been studied extensively.^{2,51-53,61,85,96-99} However, in previous studies, the cationic moiety is attached to poly(oxyethylene) spacer groups that provide flexibility independent of the cellulose chain.⁵⁰ We have prepared mono and diquatarnary aminoalkylcarbamoyl cellulose derivatives as graft copolymers having a defined charge density where the quaternary nitrogen is located at the sites of carboxymethylation of the starting polymer.^{64,65} The degree of substitution of the carboxymethyl cellulose was 0.70 and the degree of substitution of the aminoamide derivative was 0.56.^{66,100} These model polymers have been used to determine the behavior of complexes formed between the charged polymer and oppositely charged

micelles of sodium dodecyl sulfate (SDS). The interaction of these novel polymers with SDS micelles has been compared with the behavior of Polyquaternium 10. Polyquaternium 10 is a quaternized hydroxyethyl cellulose derivative with the quaternary nitrogen located at the end of a poly(oxyethylene) graft ⁵⁰ (Figure 1.7). The interactions of Polyquaternium 10 with anionic surfactants have been studied extensively by surface tension, precipitation pattern, dye solubilization, electrophoresis and changes in foam stability.^{51-53,61,89,90,101}

4.4 EXPERIMENTAL

Pseudo phase diagrams were prepared for the following system: SDS / Polymer / water. These phase diagrams were used to determine where charge neutralization occurred. The solutions were prepared by addition of a concentrated polymer solution (3%) to a solution of SDS. The samples were shaken, placed in an oven at 60°C for 8 hours, and allowed to cool slowly. The appearance of the liquid and precipitate was judged visually following the method of Goddard and Hannan.^{52,90}

4.5 RESULTS AND DISCUSSION

The complexation of Polyquaternium 10 and two aminoalkylcarbamoyl cellulose graft co-polymers with SDS was studied by precipitation above and below the critical micelle concentration (CMC) of SDS, 2.4 mg/ml.¹⁰²⁻¹⁰⁵ The cellulosic derivatives (Figure 1.8) used were 2-trimethylammoniummethyl carbamoylmethyl cellulose iodide (MQNNED) which has one cationic charge per graft and 3-trimethylammonium-2-hydroxypropyl-N,N-dimethylammoniummethyl carbamoylmethyl cellulose chloride (DQNNED) which has two cationic charges per graft. The counterion for MQNNED was changed from iodine to chlorine by dialysis with sodium chloride.

The pseudo phase diagrams of SDS / water / Polymer (Figures 4.4–4.6) show the formation of clear solutions at low concentrations of SDS. Increases in solution viscosity were observed along with formation of turbid or hazy solutions, precipitates and gels as the percentage of SDS was increased. At high surfactant concentrations, resolubilization of the polymers was observed. These results are in agreement with previous studies of complexation of anionic surfactants and Polyquaternium 10.^{52,90}

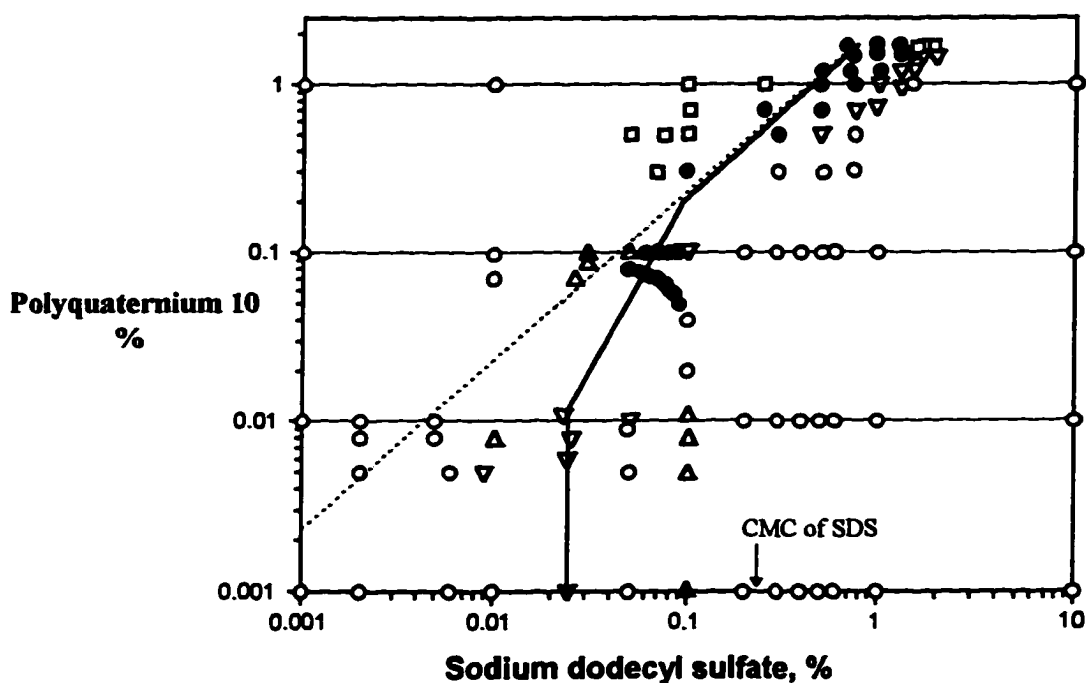


Figure 4.4: Pseudo Phase Diagram of the System Polyquaternium 10 / Sodium Dodecyl Sulfate / Water. Symbols indicate: O clear solution; ● precipitate; ▽ slight precipitate; Δ hazy solution; □ gel; - - - - - theoretical charge neutralization; and ——— maximum precipitate observed.

The complexation of cationic polymers with anionic surfactants proceeds via charge neutralization⁹⁰ (Eq. 4.1).



where P is the cationic polymer containing n cationic charges per residue molecular weight and D⁻ is the anionic surfactant containing one anionic charge per residue molecular weight. Theoretical charge neutralization occurs at a 1 : 1 ratio of cationic and anionic charges resulting in maximum precipitation of the polymer.

For Polyquaternium 10, the charge density or average residue molecular weight per cationic charge is 689 g/mol while the charge density of SDS is 288 g/mol. Therefore, theoretical charge neutralization should occur at a weight ratio of 2.3 : 1. Comparison of the observed maximum precipitation with the theoretical charge neutralization for this system (Figure 4.4) indicates that this relationship holds true for concentrations of polymer and surfactant ≥ 0.200 and 0.100%, respectively. At polymer concentrations $< 0.200\%$, the concentration of SDS necessary to precipitate the Polyquaternium10-SDS complex is independent of polymer concentration. This result agrees with results observed previously for Polyquaternium 10 and SDS.^{52,90}

The average molecular weight per cationic charge for MQNNED is approximately 467 g/mol.; therefore, theoretical charge neutralization should occur at a weight ratio of 1.6 : 1. The results for this system (Figure 4.5) indicate that this relationship holds true for concentrations of polymer and surfactant ≥ 0.020 and 0.015%, respectively. At polymer concentrations $\leq 0.010\%$, the concentration of SDS necessary to precipitate the MQNNED-SDS complex is independent of polymer concentration.

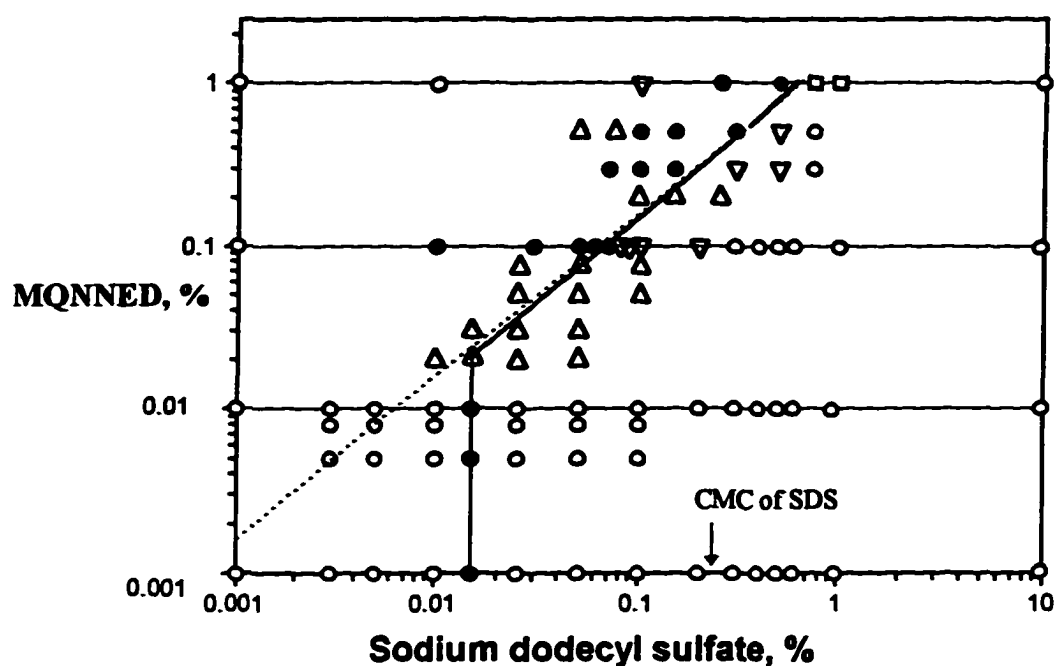


Figure 4.5: Pseudo Phase Diagram of the System MQNNED / Sodium Dodecyl Sulfate / Water. Symbols indicate: O clear solution; ● precipitate; ▽ slight precipitate; Δ hazy solution; □ gel; - - - - - theoretical charge neutralization; and ——— maximum precipitate observed.

The average molecular weight per cationic charge for DQNNED is approximately 569 g/mol.. Since the graft on DQNNED contains two cationic charges, two theoretical charge neutralization weight ratios can be calculated. The first weight ratio, 2.0 : 1, is related to the addition of one SDS molecule per two cationic charges. The second weight ratio, 1 : 1, is related to the addition of two SDS molecules per two cationic charges. The results (Figure 4.6) indicate that maximum precipitation of the DQNNED-SDS complex occurs between these two theoretical charge neutralization

lines. Therefore, for concentrations of polymer and surfactant $\geq 0.010\%$, the DQNNED-SDS complex precipitates maximally when approximately 1.5 SDS molecules neutralize the charge of the 2 cationic sites. At low polymer concentrations ($< 0.010\%$) the concentration of SDS necessary to precipitate the DQNNED-SDS complex is independent of polymer concentration.

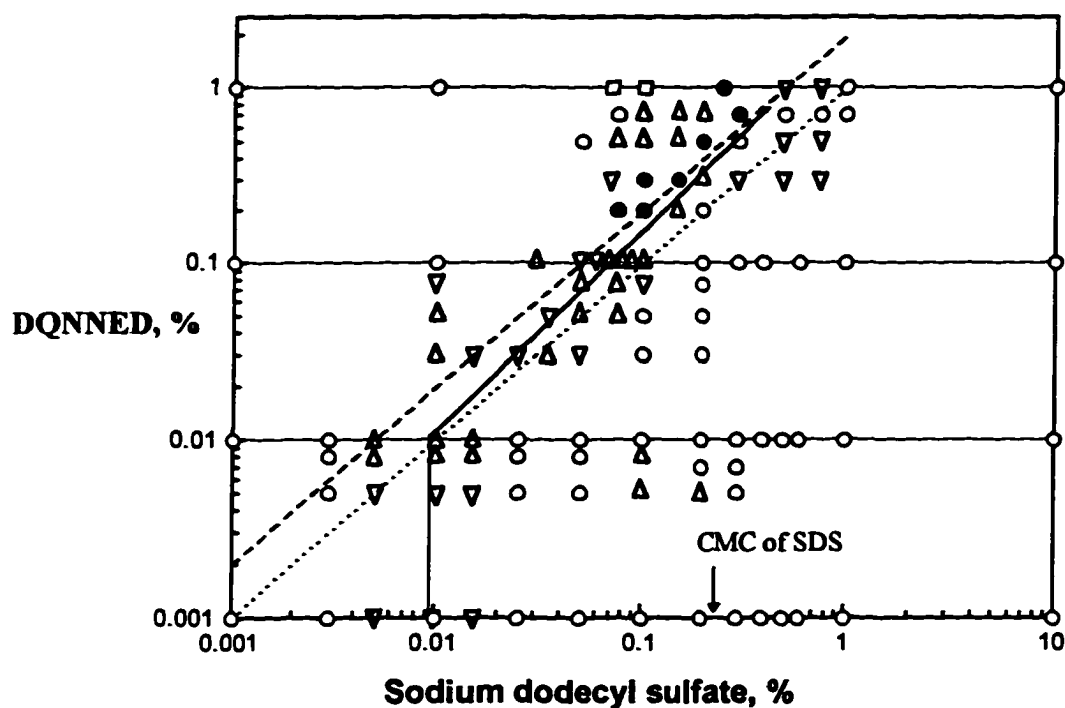


Figure 4.6: Pseudo Phase Diagram of the System DQNNED / Sodium Dodecyl Sulfate / Water. Symbols indicate: O clear solution; ● precipitate; ▽ slight precipitate; Δ hazy solution; □ gel; - - - - - theoretical charge neutralization for 1 SDS;theoretical charge neutralization for 2 SDS; and ——— maximum precipitate observed.

The observed maximum precipitation patterns for the three systems is shown (Figure 4.7). The results indicate that the polymers precipitate at their respective theoretical charge neutralization ratio when the concentrations of polymer are ≥ 0.010 , 0.020 and 0.200% for DQNNED, MQNNED and Polyquaternium 10, respectively. However, at polymer concentrations $\leq 0.010\%$, the limiting SDS concentration necessary to precipitate increases as the structure of the polymer is varied: DQNNED-SDS < MQNNED-SDS < Polyquaternium 10-SDS. Therefore, when precipitation is independent of polymer concentration, a polyelectrolyte containing two cationic charges per residue will precipitate at a lower percent SDS than its monoquaternary analog, and a monoquat closely related with the backbone will precipitate before a monoquat attached to a flexible spacer arm.

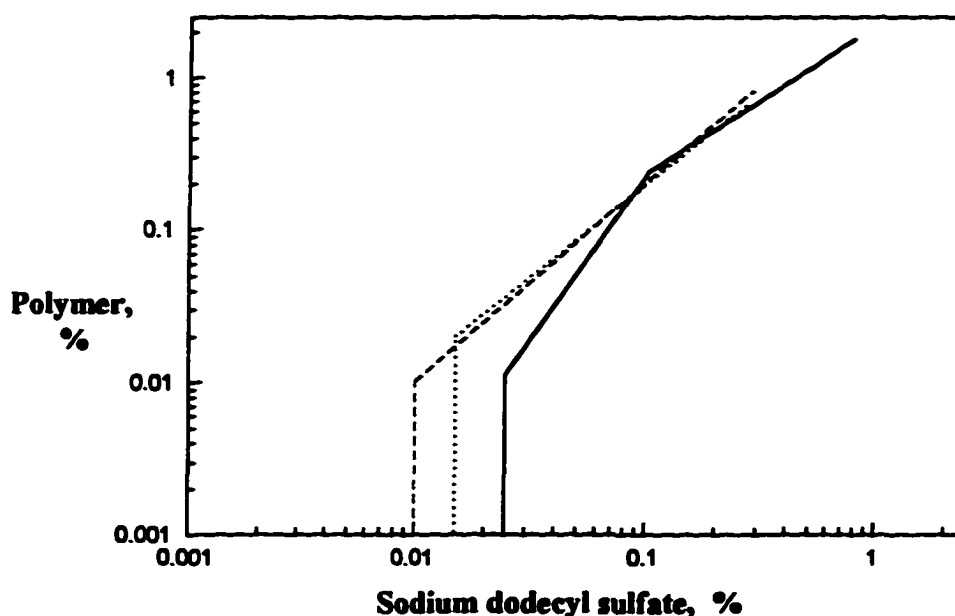


Figure 4.7: Observed Maximum Precipitation Pattern for the Three Systems.
 Symbols indicate: - - - - DQNNED; MQNNED; and
 ——— Polyquaternium 10

4.5 CONCLUSIONS

All three polymers studied precipitate at their respective theoretical charge neutralization ratio when the concentrations of polymer and anionic surfactant are greater than 0.010%. However, at polymer concentrations less than 0.010%, a fixed concentration of sodium dodecyl sulfate is necessary to precipitate the complexes. The magnitude of the fixed concentration decreases as the charge density of the polymer increases.

CHAPTER 5

RESOLUBILIZATION WITH MIXED MICELLES

5.1 INTRODUCTION

Surfactants used in practical applications essentially always consist of a mixture of surface active compounds.¹⁰⁶ The use of mixed surfactant systems results from the cost of pure surfactants and the small performance advantages of pure surfactants over mixtures. In many applications, such as cosmetics and household products, mixtures of surfactants are found to exhibit superior properties over systems containing pure surfactants. Some physical properties of surfactants are surface tension, wetting power, foam height, and irritation potential. Anionic surfactants are widely used due to their superior foaming properties and low cost. However, these surfactants can be irritating to the skin and eyes. Cationic surfactants foam well, have adequate cleaning power, and provide antistat properties. However, with repeated use, cationic surfactants may build up on the surface of the material being cleaned forming a type of soil. Nonionic surfactants are used as foam boosters and stabilizers in emulsions due to their mildness. They are auxiliary surfactants since they do not exhibit sufficient cleansing power to be considered principal detergents.

5.2 POLYMER SURFACTANT BINDING

The solubility behavior of cationic polyelectrolytes and anionic surfactants is complex. As shown previously (Chapter 4) at low concentrations of SDS, the polymer solution remains clear, but changes in viscosity along with the formation of hazy solutions, precipitated material and gels occur as the concentration of SDS is increased. If the surfactant concentration is sufficiently high, resolubilization of the precipitated material occurs. At polymer concentrations of 0.01% or greater, maximum precipitation corresponds to a stoichiometric charge neutralization of the cationic polymer.

Dubin and coworkers¹⁰⁷⁻¹¹⁶ have examined the effect of adding a nonionic surfactant on precipitation of polymer-surfactant complexes. This group has determined, that at a certain ionic strength and ratio of anionic/nonionic surfactant, precipitation can be inhibited (i.e. the precipitated material can be resolubilized). By diluting an ionic surfactant with a nonionic surfactant, the interaction with oppositely charged polyelectrolytes can be moderated.^{107-111,113-116} The interaction and phase behavior of the systems can be controlled by the mole fraction of ionic surfactant, Y , and the ionic strength of the solution, I . Complex formation takes place only above a critical mole fraction of ionic surfactant, Y_C , and there is a direct relationship between Y_C and $I^{1/2}$ which is independent of polymer and surfactant concentration.^{88,107,112,115} There are two types of soluble aggregates formed in these systems: intra- and intermolecular. Intramolecular aggregates involve only one polymer chain with the micelles while intermolecular aggregates involve several chains with the same micelle (Figure 5.1).^{107,111,113,115} Intermolecular aggregates are formed at high polymer concentrations and when the molecular weight of the polymer is very high.

Factors affecting polymer-surfactant association are the micelle surface charge density (σ) polymer linear charge density (ξ) and the Debye-Hückel ion atmosphere thickness (K^{-1}).¹¹⁶ The corresponding experimental variables are the mole fraction of charged monomers in the micelle (Y_{SDS}) structural polymer charge density ($1/b$) where b is the distance between charges on the polymer backbone, and the ionic strength of the solution (I)¹¹⁶ (Figure 5.2). The flexibility of the polyelectrolyte is believed to be another factor.⁸⁸

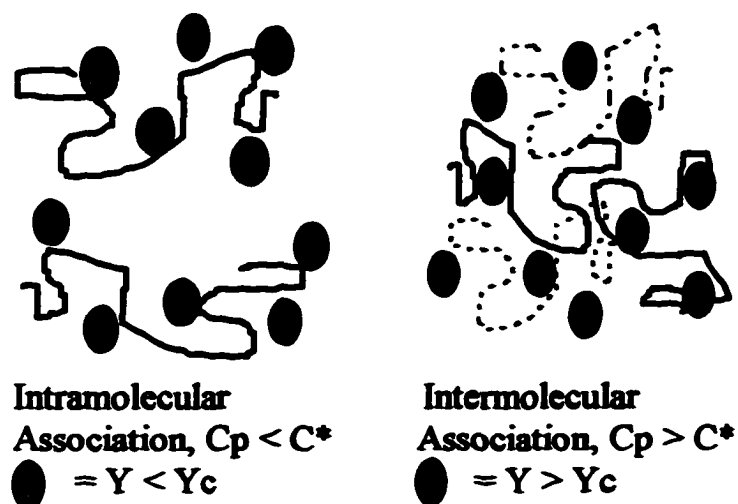


Figure 5.1: Intra and Intermolecular Aggregation. The Two Extreme Conditions.

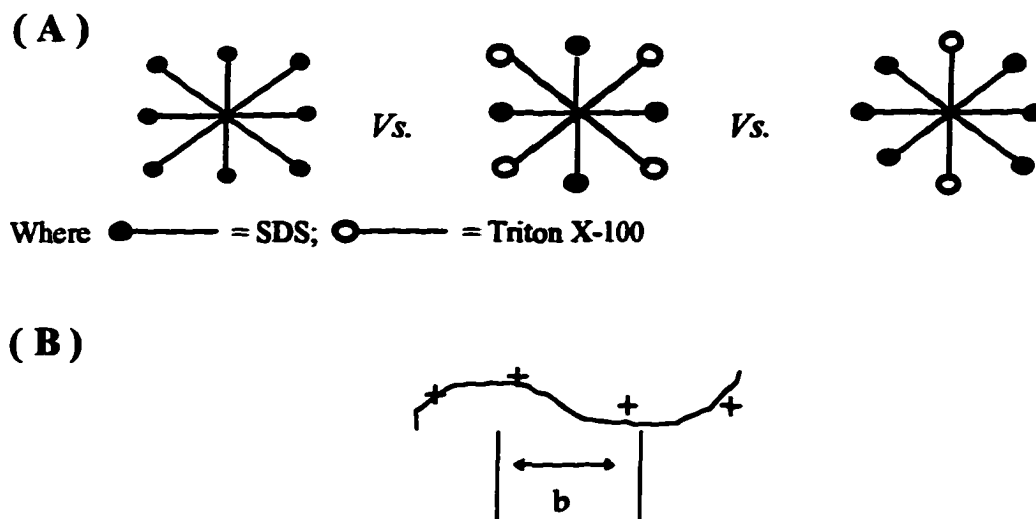


Figure 5.2: Factors Affecting Association: (A) Y_{SDS} = fraction of charged monomers in micelle; (B) $1/b$ is the structural polymer charge density.

For a given polyelectrolyte at constant I and b , a critical mole fraction, Y_C , corresponding to a critical micelle surface charge density may be determined.¹¹⁶ Y_C corresponds to the reversible formation of soluble polyelectrolyte-mixed surfactant micelle complexes as determined by initial increase in solution turbidity. For $Y < Y_C$, no polymer-polymer association takes place regardless of polymer or surfactant concentration.^{107,108,111,116} Beyond this phase transition, soluble complexes, liquid coacervate or amorphous precipitate may be formed.¹¹⁷ The complex phase depends on polymer concentration, surfactant concentration, molecular weight, micelle surface charge density, polymer linear charge density and ionic strength.^{109,117}

5.3 CMC OF MIXING

Surfactants vary in their tendency to form aggregates such as micelles, precipitates and monolayers.¹⁰⁶ The addition of a nonionic surfactant to an anionic surfactant enhances the formation of micelles. The critical micelle concentration (CMC) is the lowest surfactant concentration at which micelles form. The lower the CMC, the greater is the tendency of the surfactant to form micelles.

In a system composed of two similar surfactants, the CMC of mixing can be modeled by assuming the thermodynamics of mixing in micelles obeys ideal solution theory.¹⁰⁶ At equilibrium, the total monomer concentration, C_M , can be determined (Eq. 5.1).

$$C_M = (CMC_A \cdot CMC_B) / (Y_A \cdot CMC_B + Y_B \cdot CMC_A) \quad (5.1)$$

where CMC_A and CMC_B are the individual CMC values of species A and B, and Y_A , Y_B are the mole fractions of the surfactants.

The micellar mole fractions, X_A and X_B , may then be calculated (Eq. 5.2):

$$X_A = Y_A \cdot C_M / CMC_A \quad \text{and} \quad X_B = Y_B \cdot C_M / CMC_B \quad (5.2)$$

If the total surfactant concentration (C_s) in the mixed system is at the CMC (i.e. an infinitesimal number of micelles are present), then C_M equals the CMC of the mixture as calculated using Eq. 5.1.

Negative deviation from ideality results for mixtures of ionic/nonionic, anionic/cationic, and zwitterionic/anionic surfactants.¹⁰⁶ In these systems the CMC of mixing is significantly lower than predicted by Eq. 5.1 due to enhanced micelle formation. When a nonionic surfactant monomer is inserted into an anionic or cationic micelle, the nonionic hydrophilic group separates the charged hydrophilic groups and decreases electrical repulsion in the Stern layer of the micelle. This separation of charge enhances micelle formation and the CMC of mixing is less than the CMC of ideal mixed micelle formation. The interactions in these systems may be described by regular solution theory (5.3 and 5.4).

$$1 = \{ Y_A \cdot X_B \cdot CMC_B \exp [W(X_A^2 - X_B^2) / RT] / Y_B \cdot X_A \cdot CMC_A \} \quad (5.3)$$

$$C_M = \{ X_B \cdot CMC_B \exp [W \cdot X_A^2 / RT] / Y_B \} \quad (5.4)$$

where W is an interaction parameter, R is the gas constant, and T is absolute temperature. If the total surfactant concentration in the mixed system is at the CMC, then C_M equals the CMC of the mixture as calculated using Eq. 5.4.¹⁰⁶

Equations 5.3 and 5.4 do not give *a priori* predictions as the interaction parameter, W , is needed.¹⁰⁶ Therefore, a value for the CMC of mixing must be determined experimentally in order to substitute for C_M in equation 5.4 and calculate W .

5.4 EXPERIMENTAL

Phase diagrams were prepared for systems of Polymer / SDS / Triton X-100 varying the ratio of surfactants in order to resolubilize the precipitated material and select samples for use in fluorescence and dynamic light scattering studies. The solutions were prepared by addition of a concentrated polymer solution to a solution of SDS and/or Triton X-100 varying the ratio of surfactants from 0-0.06% or 0-1% (w/v) and maintaining a constant polymer concentration of either 0.1 or 1% (w/v). The samples were shaken, placed in an oven at 60°C for 8 hours, and allowed to cool slowly. The appearance of the liquid and precipitate was judged visually following the method of Goddard and Hannan.^{52,90} Reduced Triton X-100 was used in place of Triton X-100 in order to remove fluorescence properties of this compound (Figure 5.3).

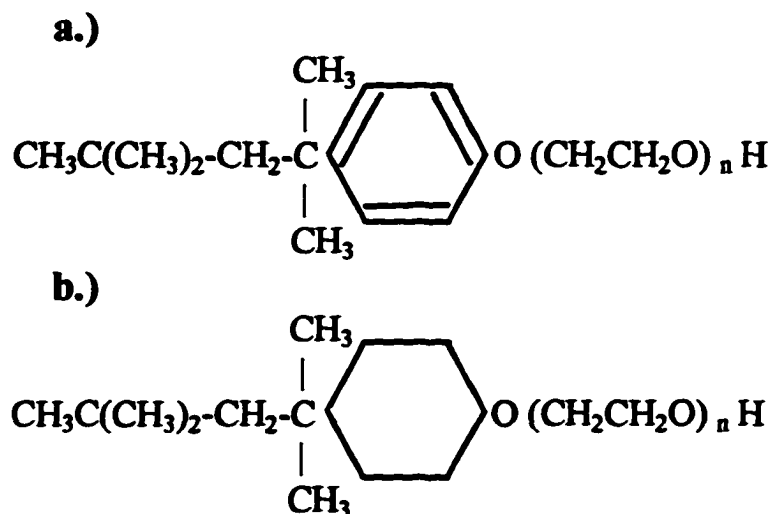


Figure 5.3: Structure of Triton X-100 and Reduced Triton X-100, n = 5 to 15; average n = 10; a.) Triton X-100 and b.) Reduced Triton X-100.

5.5 RESULTS AND DISCUSSION

5.5.1: 0.1% Polymer and 0.06% Total Surfactant Concentration

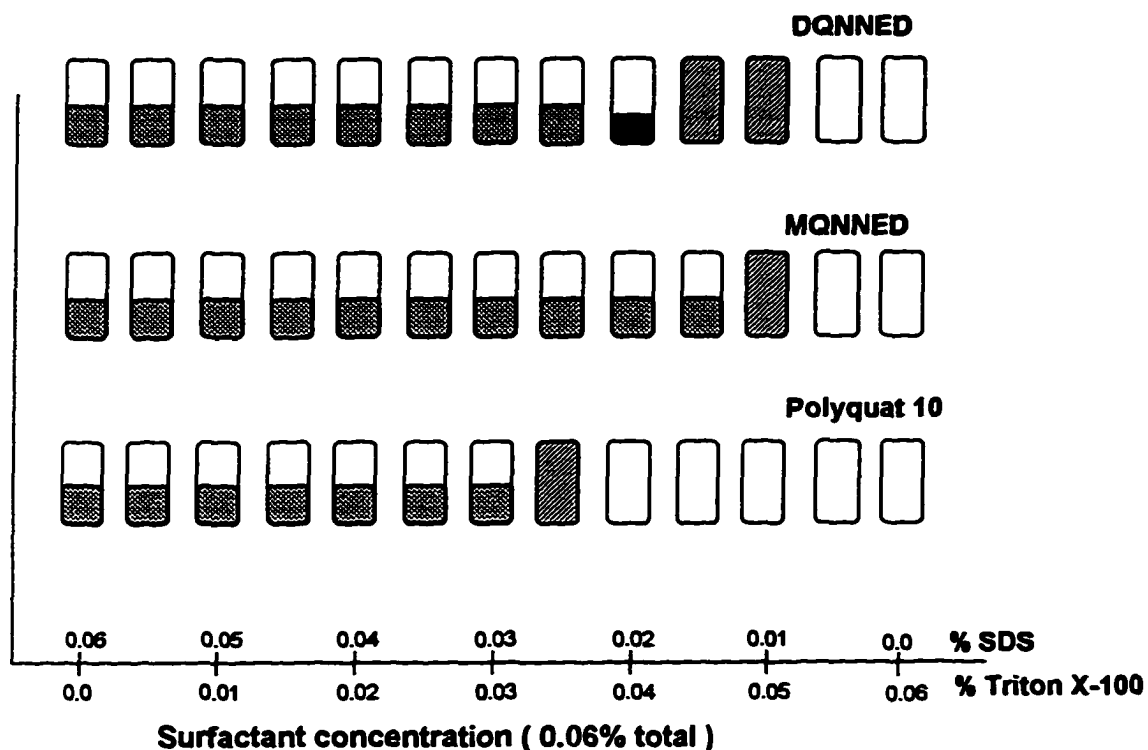
The precipitation pattern of systems of 0.1% polymer / SDS / Triton X-100 were studied by varying the percentage of anionic SDS from 0-0.06% (w/v) at constant polymer concentration. A polymer concentration of 0.1% (w/v) was chosen to be in the region of maximum precipitation below the critical overlap concentration, c^* , of the polymers. The purpose was to determine the critical mole fraction of SDS, Y_C for binding of the mixed surfactant micelles with the cationic polymers below the critical micelle concentration of SDS.

The results of this study (Figure 5.4) indicate that at concentrations of SDS $\geq 0.025\%$, ($Y_{SDS} \geq 0.62$) precipitation occurs for the Polyquaternium 10 - mixed surfactant micelle complexes. The charge density on the micelles causes them to bind strongly resulting in the onset of precipitation of the complex due to charge neutralization. At concentrations of SDS $\leq 0.020\%$ ($Y_{SDS} \leq 0.53$), single phase, clear solutions were observed. Therefore, $Y_C = 0.62$ for the system (Table 5.1).

For MQNED and DQNED mixed micelle complexes, two phase systems exist when the concentration of SDS is $\geq 0.010\%$ ($Y_{SDS} \geq 0.31$). At concentrations of SDS $\leq 0.005\%$ ($Y_{SDS} \leq 0.17$), single phase, clear solutions were observed. Therefore, $Y_C = 0.31$ for these systems (Table 5.1).

At low concentrations of polymer and surfactant, the critical mole fraction of SDS necessary to cause the onset of precipitation is influenced by a flexible spacer

group. The complexes of Polyquaternium 10 - mixed surfactant micelles can support a higher micelle charge density than either of the quaternary derivatives closely associated



Symbols indicate:





-  clear precipitate and clear supernatant;
-  white precipitate and clear supernatant;
-  hazy solution; and
-  clear one phase solution.

Figure 5.4: Phase Diagrams for the Systems 0.1% Polymer / Sodium Dodecyl Sulfate / Triton X-100 Varying the Ratio of the Two Surfactants.

Table 5.1: Data for Mixed Micelles of Sodium Dodecyl Sulfate and Triton X-100, 0.1% Polymer.

| SDS % | Triton X-100 % | SDS mM | Triton X-100 mM | Cs Total mM | Y _{SDS} | Y _{Triton X-100} | Cm* mM | X _{SDS} | X _{Triton X-100} | Is Cs Total ≥ Cm* ? |
|----------|-------------------|-----------|--------------------|----------------|------------------|---------------------------|-----------|------------------|---------------------------|------------------------|
| 0.060 | 0.000 | 2.08 | 0.00 | 2.08 | 1.00 | 0.00 | 8.00 | 1.000 | 0.000 | no |
| 0.055 | 0.005 | 1.91 | 0.08 | 1.99 | 0.96 | 0.04 | 3.46 | 0.415 | 0.585 | no |
| 0.050 | 0.010 | 1.74 | 0.15 | 1.89 | 0.92 | 0.08 | 2.13 | 0.244 | 0.756 | no |
| 0.045 | 0.015 | 1.56 | 0.23 | 1.79 | 0.87 | 0.13 | 1.49 | 0.162 | 0.838 | yes |
| 0.040 | 0.020 | 1.39 | 0.31 | 1.70 | 0.82 | 0.18 | 1.12 | 0.114 | 0.886 | yes |
| 0.035 | 0.025 | 1.22 | 0.39 | 1.60 | 0.76 | 0.24 | 0.87 | 0.083 | 0.917 | yes |
| 0.030 | 0.030 | 1.04 | 0.46 | 1.51 | 0.69 | 0.31 | 0.70 | 0.061 | 0.939 | yes |
| 0.025 | 0.035 | 0.87 | 0.54 | 1.41 | 0.62 | 0.38 | 0.57 | 0.044 | 0.956 | yes |
| 0.020 | 0.040 | 0.69 | 0.62 | 1.31 | 0.53 | 0.47 | 0.47 | 0.031 | 0.969 | yes |
| 0.015 | 0.045 | 0.52 | 0.70 | 1.22 | 0.43 | 0.57 | 0.39 | 0.021 | 0.979 | yes |
| 0.010 | 0.050 | 0.35 | 0.77 | 1.12 | 0.31 | 0.69 | 0.33 | 0.013 | 0.987 | yes |
| 0.005 | 0.055 | 0.17 | 0.85 | 1.02 | 0.17 | 0.83 | 0.28 | 0.006 | 0.994 | yes |
| 0.000 | 0.060 | 0.00 | 0.93 | 0.93 | 0.00 | 1.00 | 0.23 | 0.000 | 1.000 | yes |

where Cs is the concentration of surfactant, Y is the mole fraction of surfactant, Cm* is the total monomer concentration from ideal solution theory as a value for mixed CMC was not available, and X is the micellar mole fraction of surfactant.

with the cellulose backbone. Below the critical overlap concentration, the critical mole fraction of SDS necessary to onset precipitation does not appear to be influenced by the number of cationic charges on the graft. Both the monoquaternary polymer, MQNNED, and the diquaternary polymer, DQNNED, require similar micelle charge densities to cause precipitation.

5.5.2: 1% Polymer and 1% Total Surfactant Concentration

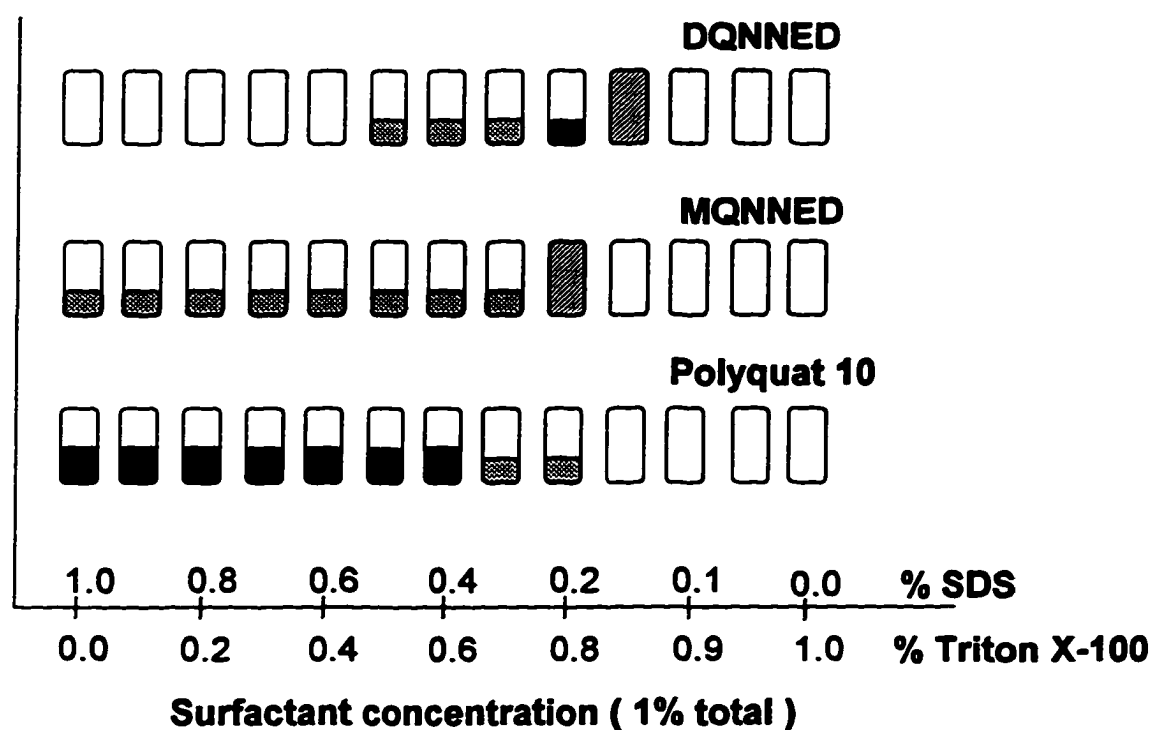
The precipitation pattern of systems of 1% polymer / SDS / Triton X-100 were studied by varying the percentage of anionic SDS from 0–1% (w/v) at constant polymer concentration. A polymer concentration of 1% (w/v) was chosen to be in the region between charge neutralization and resolubilization which is above the critical overlap concentration, c^* . The purpose was to determine the critical mole fraction of SDS, Y_C , for binding of the mixed surfactant micelles with the cationic polymers above the critical micelle concentration of SDS.

The results of this study (Figure 5.5 and 5.6) indicate that at concentrations of $\text{SDS} \geq 0.15\%$, precipitation occurs for both Polyquaternium 10- and MQNNED- mixed surfactant micelle complexes. The high charge density on the micelles causes them to bind strongly resulting in the onset of precipitation of the complex due to charge neutralization. At concentrations of $\text{SDS} \leq 0.15\%$ ($Y_{\text{SDS}} \leq 0.28$), single phase, clear solutions were observed. Therefore, $Y_C = 0.30$ for the systems of Polyquaternium 10- and MQNNED- mixed surfactant micelle complexes (Table 5.2).

For DQNNED, two phase systems exist when the concentration of SDS is between 0.50% and 0.11%. The charge density on the micelles is high enough to cause

precipitation of the complex but not sufficiently high to resolubilize the complex.

Interestingly, there are two distinct regions where one phase, clear solutions exist.



Symbols indicate:





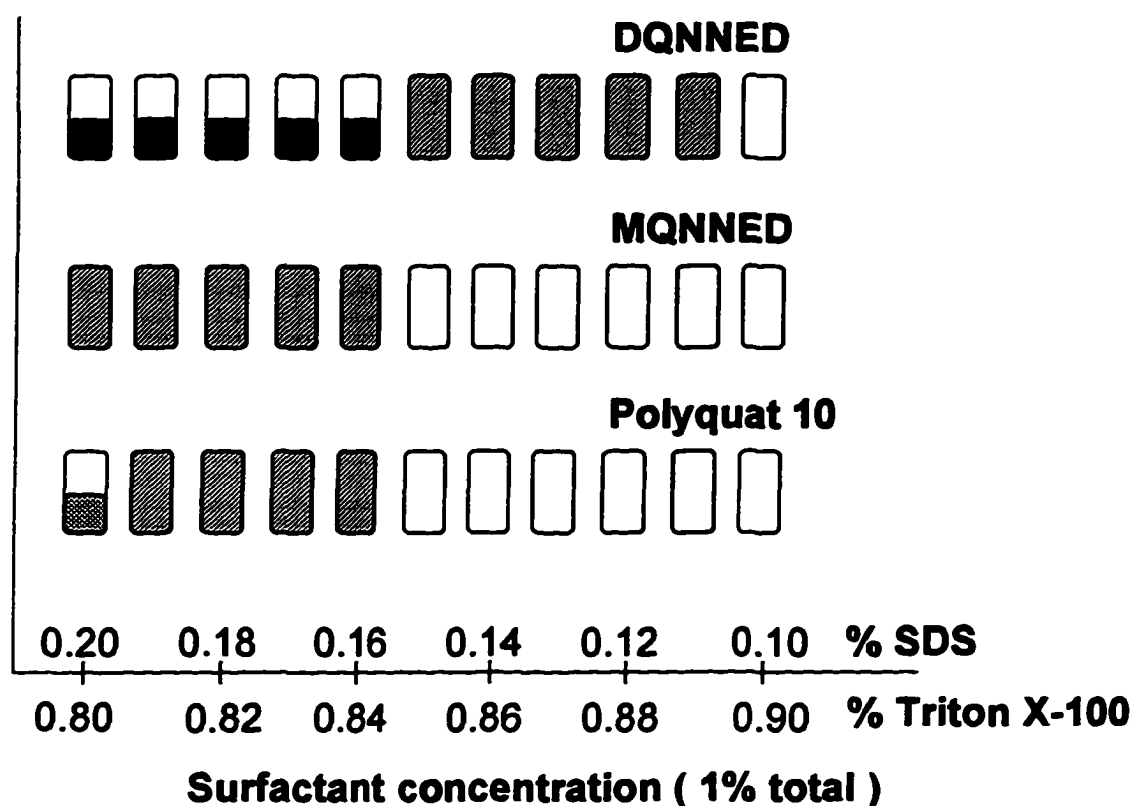
-  clear precipitate and clear supernatant;
-  white precipitate and clear supernatant;
-  hazy solution; and
-  clear one phase solution.

Figure 5.5: Phase Diagram for the Systems 1% Polymer / Sodium Dodecyl Sulfate / Triton X-100 Varying the Ratio of the Two Surfactants. Concentration of SDS Varies Between 0.0 and 1.0%.



Symbols indicate:





-  clear precipitate and clear supernatant;
-  white precipitate and clear supernatant;
-  hazy solution; and
-  clear one phase solution.

Figure 5.6: Phase Diagram for the Systems 1% Polymer / Sodium Dodecyl Sulfate / Triton X-100 Varying the Ratio of the Two Surfactants. Concentration of SDS Varies Between 0.10 and 0.20% to Accurately Determine Y_C

Table 5.2: Data for Mixed Micelles of Sodium Dodecyl Sulfate and Triton X-100, 1.0% Polymer.

| SDS % | Triton X-100 % | SDS mM | Triton X-100 mM | Cs Total mM | Y_{SDS} | Y_{Triton X-100} | Cm* mM | X_{SDS} | X_{Triton X-100} | Is Cs Total ≥ Cm*? |
|------------------|---------------------------|-------------------|----------------------------|------------------------|------------------------|---------------------------------|-------------------|------------------------|---------------------------------|-------------------------------|
| 1.00 | 0.00 | 34.72 | 0.00 | 34.72 | 1.00 | 0.00 | 8.00 | 1.000 | 0.000 | yes |
| 0.90 | 0.10 | 31.25 | 1.55 | 32.80 | 0.95 | 0.05 | 3.09 | 0.368 | 0.632 | yes |
| 0.80 | 0.20 | 27.78 | 3.09 | 30.87 | 0.90 | 0.10 | 1.83 | 0.205 | 0.795 | yes |
| 0.70 | 0.30 | 24.31 | 4.64 | 28.94 | 0.84 | 0.16 | 1.25 | 0.131 | 0.869 | yes |
| 0.60 | 0.40 | 20.83 | 6.18 | 27.02 | 0.77 | 0.23 | 0.92 | 0.088 | 0.912 | yes |
| 0.50 | 0.50 | 17.38 | 7.73 | 25.09 | 0.69 | 0.31 | 0.70 | 0.081 | 0.939 | yes |
| 0.40 | 0.60 | 13.89 | 9.27 | 23.16 | 0.60 | 0.40 | 0.55 | 0.041 | 0.959 | yes |
| 0.30 | 0.70 | 10.42 | 10.82 | 21.24 | 0.49 | 0.51 | 0.44 | 0.027 | 0.973 | yes |
| 0.20 | 0.80 | 6.94 | 12.36 | 19.31 | 0.36 | 0.64 | 0.35 | 0.016 | 0.984 | yes |
| 0.19 | 0.81 | 6.60 | 12.52 | 19.12 | 0.35 | 0.65 | 0.35 | 0.015 | 0.985 | yes |
| 0.18 | 0.82 | 6.25 | 12.67 | 18.92 | 0.33 | 0.67 | 0.34 | 0.014 | 0.986 | yes |
| 0.17 | 0.83 | 5.90 | 12.83 | 18.73 | 0.32 | 0.68 | 0.33 | 0.013 | 0.987 | yes |
| 0.16 | 0.84 | 5.56 | 12.98 | 18.54 | 0.30 | 0.70 | 0.32 | 0.012 | 0.988 | yes |
| 0.15 | 0.85 | 5.21 | 13.14 | 18.35 | 0.28 | 0.72 | 0.32 | 0.011 | 0.989 | yes |
| 0.14 | 0.86 | 4.86 | 13.29 | 18.15 | 0.27 | 0.73 | 0.31 | 0.010 | 0.990 | yes |
| 0.13 | 0.87 | 4.51 | 13.45 | 17.96 | 0.25 | 0.75 | 0.30 | 0.010 | 0.990 | yes |
| 0.12 | 0.88 | 4.17 | 13.60 | 17.77 | 0.23 | 0.77 | 0.30 | 0.009 | 0.991 | yes |
| 0.11 | 0.89 | 3.82 | 13.76 | 17.58 | 0.22 | 0.78 | 0.29 | 0.008 | 0.992 | yes |
| 0.10 | 0.90 | 3.47 | 13.91 | 17.38 | 0.20 | 0.80 | 0.29 | 0.007 | 0.993 | yes |
| 0.05 | 0.95 | 1.74 | 14.68 | 16.42 | 0.11 | 0.89 | 0.26 | 0.003 | 0.997 | yes |
| 0.00 | 1.00 | 0.00 | 15.46 | 15.46 | 0.00 | 1.00 | 0.23 | 0.000 | 1.000 | yes |

where Cs is the concentration of surfactant, Y is the mole fraction of surfactant, Cm* is the total monomer concentration from ideal solution theory as a value for mixed CMC was not available, and X is the micellar mole fraction of surfactant.

The first region is at high micelle charge density ($1 \leq \text{SDS} \leq 0.6\%$) and the second region at low charge density ($\text{SDS} \leq 0.10\%$). Therefore, $Y_c = 0.22$ for this system. The first region is attributed to the resolubilization of the complex by full micelles (interpolymer - micelle complexation) as this system is always above the CMC of mixing (Table 5.2). The second region is attributed to the binding of mixed surfactant micelles within the complex as the high percentage of Triton X-100 will shield the polymer molecules from each other resulting in intramolecular polymer - micelle complexation.

At high concentrations of polymer and surfactant, the critical mole fraction of SDS necessary to induce precipitation is independent of extension from the polymer chain for a monoquaternary derivative. However, the critical mole fraction of SDS necessary to induce precipitation appears to be influenced by the number of cationic charges on the graft as DQNNED requires a lower micelle charge density to precipitate than MQNNED.

5.6 CONCLUSIONS

For the polymer - mixed surfactant micelle complexes studied, the critical mole fraction of anionic surfactant necessary to cause precipitation appears to be dependent upon both flexibility of the polyelectrolyte and the number of charges on the graft. Below the critical overlap concentration, a flexible polyelectrolyte will support a higher micelle charge density than a semi-rigid polyelectrolyte. Above the critical overlap concentration, where intermolecular interactions predominate, a monoquaternary polyelectrolyte will support a higher charge density than its diquaternary analog regardless of the flexibility of the polyelectrolyte.

CHAPTER 6: PYRENE FLUORESCENCE STUDIES

6.1 INTRODUCTION

The binding of an ionic surfactant to a polyelectrolyte is expected to influence the microenvironment of both.⁹³ Surfactants affect the environment through association with the polyelectrolyte and formation of micelles. Polyelectrolytes affect the environment through conformational changes that occur in solution and association with the surfactant resulting in the formation of inter or intramolecular complexes.

Two approaches have been used to study the microenvironment formed by association of surfactants with polymers. The first approach is the addition of a fluorescent probe to the solution which will partition preferentially to the polymer-surfactant complexes, micelles or the polymer. The second approach is to covalently label the polymer with a fluorescent dye that will elucidate association phenomena occurring in the system with respect to the polymer.

6.2 CHARACTERIZATION OF POLYMER - SURFACTANT COMPLEXES

An organic dye added to polymer - surfactant solutions will reside preferentially in the hydrophobic microdomains formed in the solution.^{93,118,119} The dye may reside either inside of the hydrophobic core, adsorbed on the surface, or in the surface layer of the complex. The average locations of probes in surfactant micelles are known with a reasonable degree of confidence.^{93,118,119} However, information on the detailed location of fluorescent probes in polymer - surfactant complexes is limited. From the photophysical changes in the properties of fluorescent probe and the known behavior of the probes in various solvents and surfactant micelles, it has become possible to gain insight into the structure of the polymer-surfactant complexes.^{93,99,118-124}

6.3 PYRENE FLUORESCENCE

6.3.1 Pyrene

Pyrene (Benzo[*def*]phenanthrene) is a colorless solid whose solutions have a light blue fluorescence (Figure 6.1). This compound exhibits a medium sensitive change in the vibrational fine structure of its emission spectrum (Figure 6.2) which affects the intensity of the I_1 and I_3 bands at 372 and 383 nm, respectively.¹²⁵ This medium sensitive change, known as the Ham effect, was first used by Kalyanasundaram and Thomas to study environmental changes resulting from micellization on the structure of the pyrene emission spectrum.¹¹⁸

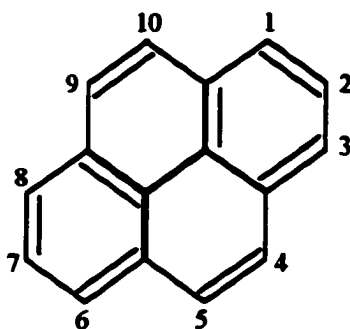


Figure 6.1: Structure of Pyrene.

6.3.2 Pyrene Fluorescence in Micellar Systems

The solvent dependence of the vibronic intensities of pyrene monomer fluorescence has been used to study micellar solutions.^{118,119} In the presence of micelles, pyrene is preferentially solubilized in the interior hydrophobic regions of the micelle.¹¹⁹ Figure 6.3 shows typical fluorescence spectra of pyrene in sodium dodecyl sulfate (SDS) both above and below the critical micelle concentration (CMC).

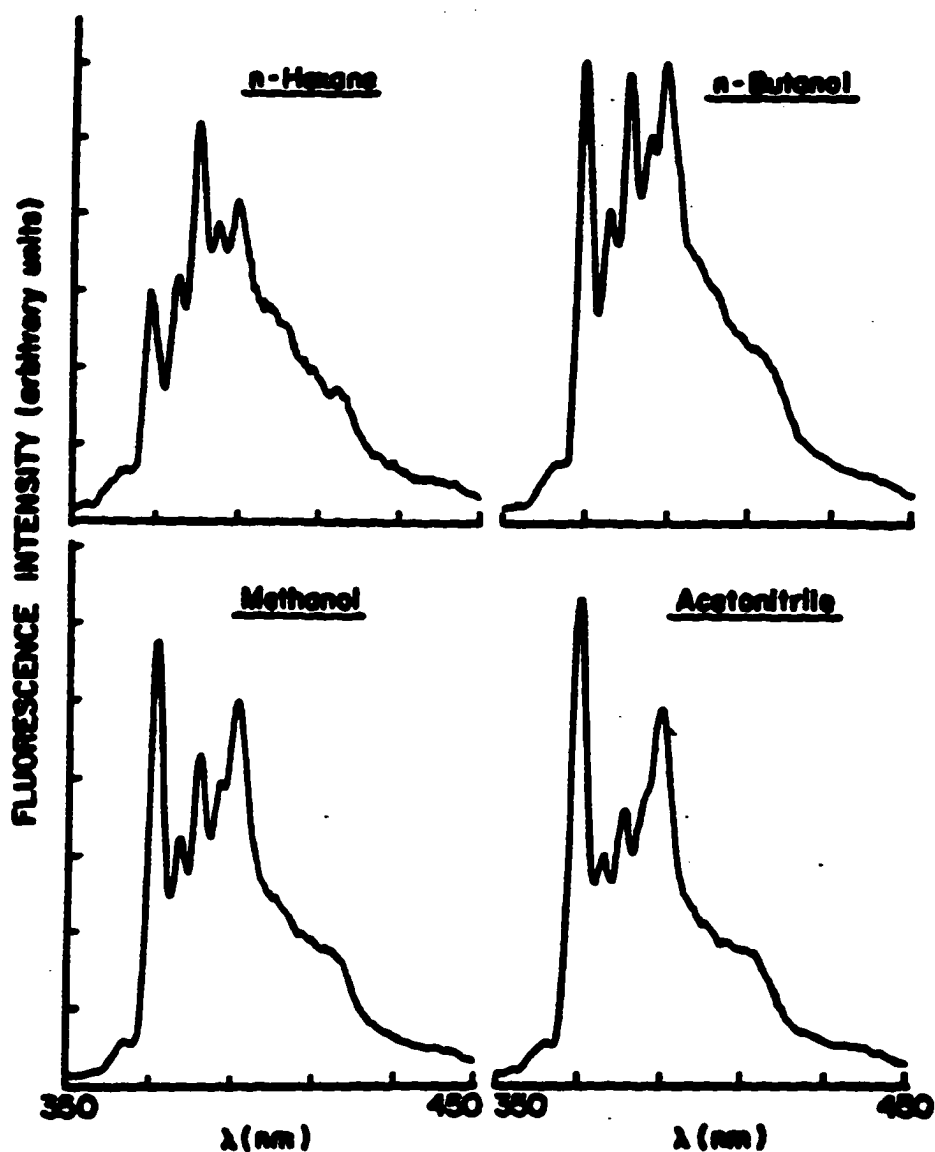


Figure 6.2: The Ham Effect. Solvent Dependence of Vibronic Band Intensities in Pyrene Monomer Fluorescence. [pyrene] = 2 μ M; $\lambda_{\text{excitation}}$ = 310 nm. The I_1 / I_3 ratio for pyrene is 1.3, 1.8, 0.6, and 1.0 for methanol, acetonitrile, n-hexane and n-butanol, respectively. (Reprinted with permission from K. Kalyanasundaram and J. K. Thomas, *Journal of the American Chemical Society*, 99(7), 2039-2044, 1977. Copyright © (1977) American Chemical Society).

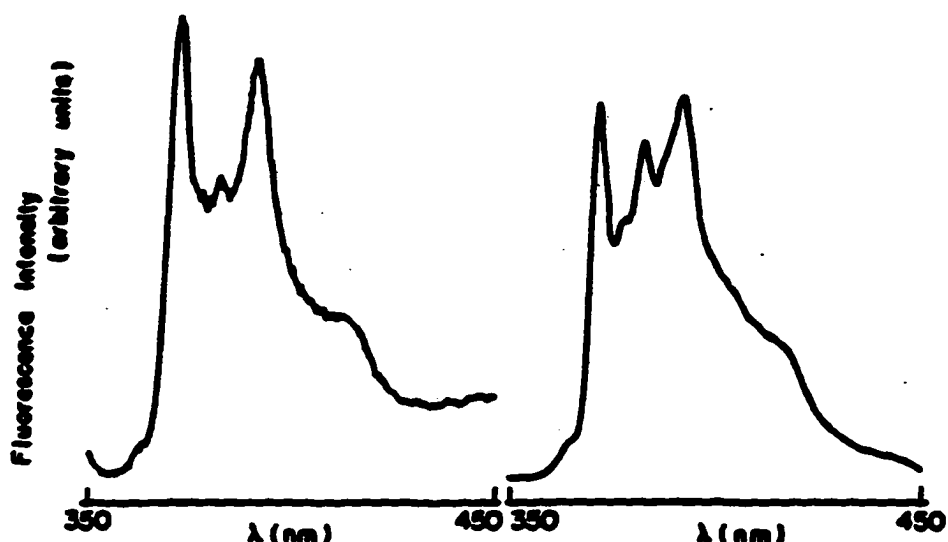


Figure 6.3: Pyrene Monomer Fluorescence in Aqueous Sodium Dodecyl Sulfate Solutions below and above the Critical Micelle Concentration; CMC = 8 mM; [pyrene] = 2 μ M. I_1 / I_3 ratio below the CMC is 1.5 and above the CMC is 1.1. (Reprinted with permission from K. Kalyanasundaram and J. K. Thomas, *Journal of the American Chemical Society*, 99(7), 2039-2044, 1977. Copyright © (1977) American Chemical Society).

Below the CMC, the I_1/I_3 band ratio is high (1.5) as micelles are not present in solution. Therefore, pyrene experiences an environment similar to water. Above the CMC, the I_1/I_3 band ratio is lower (1.1). Pyrene is now solubilized in an environment between that of an alkane and water, i.e. the hydrophobic interior of the micelles.¹¹⁹ Therefore, the ratio of the I_1/I_3 bands may be used to determine the environment in polymer-surfactant complexes provided there is no change in pyrene fluorescence spectrum due to the polymer itself.

6.3.3 Pyrene Fluorescence in Polymer - Surfactant Complexes

Winnik and Winnik¹²⁶ have studied the interactions of SDS with hydroxypropylcellulose (HPC) using pyrene fluorescence. The results of this study

indicated that a decrease in the I_1/I_3 band ratio reflected transfer of pyrene to a less polar environment when SDS was added to the system. The I_1/I_3 band ratio of pyrene was found to be independent of polymer concentration and dependent upon SDS concentration (Figure 6.4). This result indicates that the formation of polymer - surfactant complexes in the solution may be determined by this method.

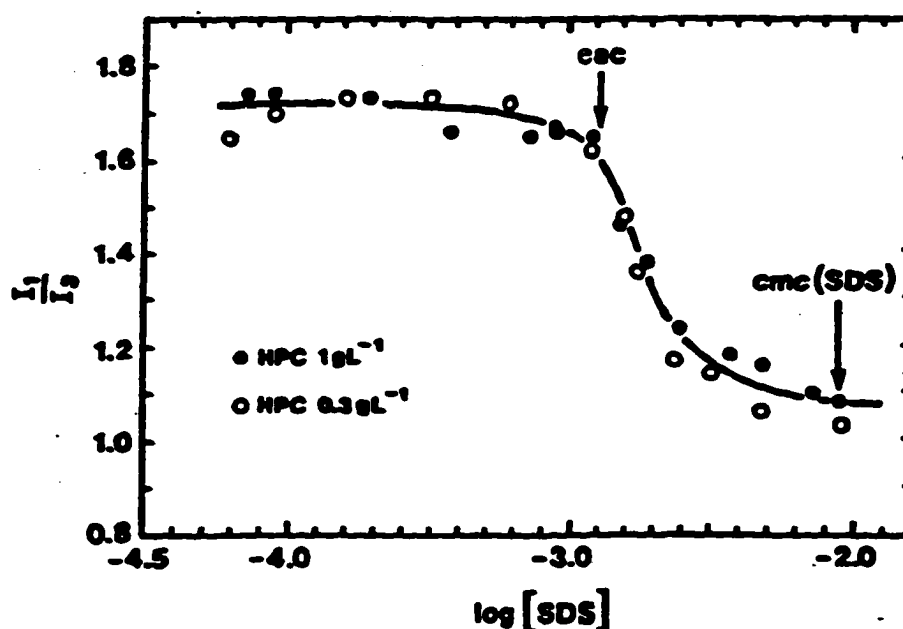


Figure 6.4: I_1/I_3 Intensity Ratio for Pyrene (3×10^{-7} M) Fluorescence in Aqueous Solutions of Hydroxypropylcellulose as a Function of Sodium Dodecyl Sulfate Concentration. (Reprinted with permission from F. M. Winnik and M. A. Winnik, *Polymer Journal*, 22(6), 482-488, 1990. Copyright © CRC Press, Boca Raton, FL.)

Saturation of the system was reached at 6.3 mM SDS corresponding to a ratio of 1.1 for pyrene which is the same value as determined by Kalyanasundaram and Thomas for micellization.¹¹⁸ The mean number of SDS clusters per polymer chain was

determined to remain constant with increasing surfactant concentration. The cluster size was determined to increase with increasing SDS concentration and decrease with increasing concentration of HPC. At concentrations of SDS greater than the CMC (8 mM) of pure SDS, the bound clusters were found to be larger in size than normal SDS micelles.

Turro *et al.*¹²³ have studied the interactions of poly(ethylene oxide) and poly(N-vinylpyrrolidone) with SDS using pyrene fluorescence. These researchers found the value of 1.8 - 1.9 for the I_1/I_3 ratio at concentrations of SDS less than 2 mM. This value was found to be independent of either the molecular weight or percentage of the polymer. In general, pyrene was found to experience a slightly more hydrophilic environment in the polymer - surfactant complexes than in normal micelles. This result was found to be consistent with the concept of smaller micelles loosely bound to the polymer chain. For smaller micelles, water penetration is expected to be greater so that the pyrene “sees” more of the polar palisade layer of the micelle and the water associated with that layer.

6.3.4 Limitations

Pyrene has a low solubility in water (2-3 μM)¹¹⁸; therefore, this probe may be added to the solution by injecting a small amount of the pyrene in a water miscible organic solvent, such as ethanol. Under these conditions microcrystals may form which will interfere in fluorescence measurements by producing excimer emission.¹²⁷ Formation of microcrystals can be avoided by preparing a filtered aqueous solution and adding the polymer and surfactant to this solution.

Oxygen present in the sample may quench the fluorescence of pyrene. In aqueous solutions, the problem is minimal as oxygen has low solubility in water (approximately 250 μM at 25 $^{\circ}\text{C}$)¹²⁸ compared to organic solvents.¹²⁹ However, quenching may occur in micellar systems¹²⁷ as the solubility of oxygen is higher in micellar solutions than in water.¹³⁰ Organic solutions may be degassed either by freeze-thawing under vacuum or by bubbling nitrogen through the solution. Unfortunately, neither technique works very well on aqueous surfactant systems as bubbles are produced. Therefore, quenching by oxygen remains a potential source of error in these systems.

6.4 EXPERIMENTAL

Fluorescence spectra of the Polymer / SDS / Triton X-100 complexes were recorded with a Fluorolog 2 Model F112X spectrofluorometer (Spex Industries). Fluorescence emission spectra were obtained at an excitation wavelength of 335 nm and emission wavelengths of 360 through 450 nm for pyrene. The bandwidths were set to 4.0 nm for excitation and 0.5 nm for emission. All measurements were performed in a 1.0 cm quartz cell at $25 \pm 1^{\circ}\text{C}$. Samples were prepared by pipetting a volume of a pyrene stock solution into each vial and evaporating the solvent (hexane) in order to obtain a final pyrene concentration of $1 \cdot 10^{-7}$ M. Next, concentrated solutions of polymer and surfactants were added to obtain final concentrations of 1% polymer and 1% total surfactant, the ratios of SDS and Triton X-100 were varied. The samples were stirred and allowed to equilibrate overnight prior to measurement. The samples were not degassed.

6.5 RESULTS AND DISCUSSION

6.5.1: 0.1% Polymer and 0.06% Total Surfactant Concentration

Pyrene is a strongly hydrophobic molecule whose water solubility is very low (2-3 mM). Changes in the vibronic fine structure intensities of the pyrene fluorescence spectra result from changes in the micro-environment encountered by the pyrene. The ratio of the I_1/I_3 bands for pyrene was high (1.8) when pyrene was solubilized in a hydrophilic medium, water. Whereas, the I_1/I_3 ratio was low (0.7) for pyrene in a hydrophobic medium, hexane, (Figure 6.5). This result agrees with previous studies of the environmental effects on vibronic band intensities in pyrene monomer fluorescence.^{118,121,123,126}

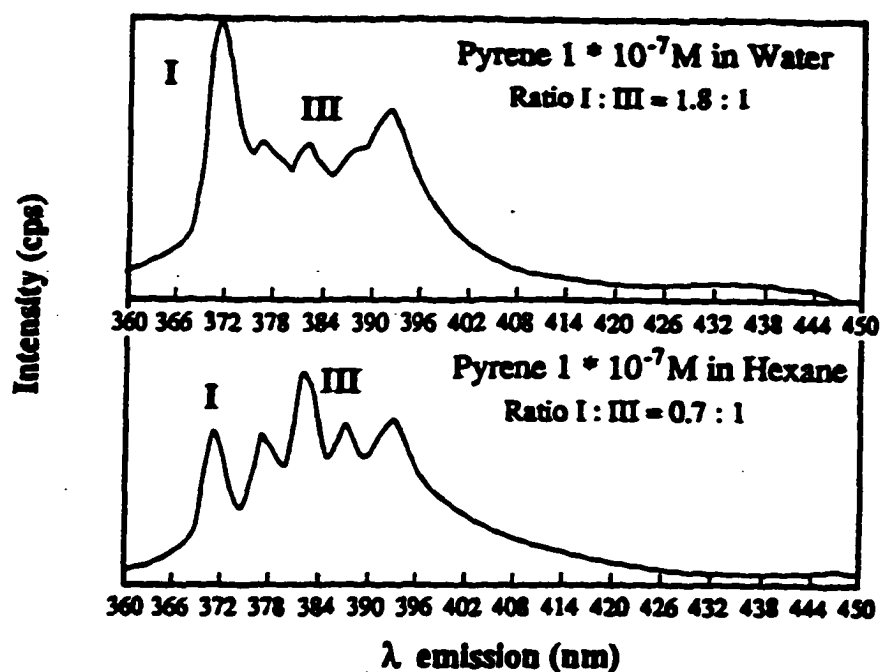


Figure 6.5: Fluorescence Intensity for Pyrene in Water and Hexane.

Aqueous solutions of the polymers, 0.1%, were examined for the presence of hydrophobic domains in polymer molecules. The I_1/I_3 ratio of the band intensities for pyrene with polymer alone indicated that pyrene was solubilized in a hydrophilic environment (Table 6.1). This ratio of 1.7 or 1.6 indicates that pyrene molecules reside in a hydrophilic environment,^{123,126} possibly the solvation shell of the polymer molecules.

Table 6.1: Fluorescence Intensity of Pyrene in Solutions of Polymer, Surfactant and Polymer - Surfactant Complexes, 0.1% Polymer.

| POLYMERS | Ratio I_1 / I_3 |
|---|-------------------------------------|
| 0.1% Polyquaternium 10 | 1.7 |
| 0.1% MQNNED | 1.6 |
| 0.1% DQNNED | 1.6 |
| SURFACTANT | |
| 0.06% Triton X-100 | 1.1 |
| 0.005% SDS 0.055% Triton X-100 | 1.1 |
| POLYMER-SURFACTANT COMPLEXES | |
| 0.1% Polyquaternium 10 & 0.06% Triton X-100 | 1.3 |
| 0.1% MQNNED & 0.06% Triton X-100 | 1.4 |
| 0.1% DQNNED & 0.06% Triton X-100 | 1.4 |
| 0.1% Polyquaternium 10 & 0.005% SDS 0.055% Triton X-100 | 1.4 |
| 0.1% MQNNED & 0.005% SDS 0.055% Triton X-100 | 1.4 |
| 0.1% DQNNED & 0.005% SDS 0.055% Triton X-100 | 1.4 |

In micellar and macromolecular systems, pyrene is preferentially solubilized in the hydrophobic regions, and the intensity of the I_1/I_3 band ratio for pyrene in micelles should decrease from that of water.¹¹⁸ If micelles are present in the surfactant solutions, the I_1/I_3 ratio should be approximately 1.1.¹¹⁸ Pyrene fluorescence intensity in solutions of 0.005% SDS / 0.055 % Triton X-100 and 0.06% Triton X-100 exhibited a I_1/I_3 ratio of 1.1 (Table 6.1). As the I_1/I_3 ratio in the micellar solutions was greater than 0.7 for hexane, the pyrene was solubilized in the hydrocarbon chain region of the micelles.

For both of these surfactant solutions, the total surfactant concentration, C_s , was greater than the CMC of mixing of the two surfactants, C_M , as previously determined (Table 5.1). For the solution of 0.005% SDS / 0.055% Triton X-100, C_s was 3.6 times greater than C_M , 1.02 mM and 0.28 mM, respectively. For the solution of 0.06% Triton X-100, C_s was 4.0 times greater than the CMC of pure Triton X-100, 0.93 mM and 0.23 mM, respectively. Therefore, pyrene fluorescence confirmed the presence of micelles in these solutions. The similarity in fluorescence intensity indicates that micelle composition at this C_s has no effect on the I_1/I_3 ratio. This type of change in pyrene emission spectrum has been well documented^{118,119,121} and has been connected to the formation of micelle clusters in both the absence^{118,119} and presence of polymer.^{120,123,124}

The single phase solutions containing 0.1% Polymer / 0.005% SDS / 0.055% Triton X-100 or 0.1% Polymer / 0.06% Triton X-100 were examined for the presence of polymer bound micelle clusters. Changes in pyrene fluorescence indicated that polymer bound micelles are present in the Polymer / SDS / Triton X-100 systems (Table 6.1). This was determined by the decrease in the I_1/I_3 band fluorescence ratio for pyrene in the complexes which indicates the formation of hydrophobic domains in these complexes.

The I_1/I_3 ratio observed for pyrene of 1.4 is higher than the ratio for pyrene solubilized in micelles alone. This slight increase in the I_1/I_3 ratio agrees with the results of previous studies which indicate that polymer - surfactant complexation has occurred.^{123,126} The pyrene solubilized in the polymer - surfactant complexes experiences a slightly more hydrophilic environment than in micelles alone which is consistent with the concept of smaller micelles being bound along the polymer strand.¹²³ For smaller micelles, one would expect the water penetration to be greater so that the pyrene would encounter more of the polar palisade layer of the micelle and the water associated with this layer.¹²³

6.5.2: 1% Polymer and 1% Total Surfactant Concentration

Aqueous solutions of the polymers, 1%, were examined for effect of high polymer concentration ($c > c^*$) on the pyrene fluorescence spectrum (i.e. presence of hydrophobic domains in polymer molecules). The I_1/I_3 ratio of the band intensities for pyrene with polymer alone indicate that pyrene was solubilized in a hydrophilic environment (Table 6.2). This ratio of 1.7 indicates that pyrene molecules reside in the solvation shell of the polymer molecules, independent of polymer concentration.

Pyrene fluorescence intensity in solutions of 0.10 % SDS / 0.90 % Triton X-100 and 1% Triton X-100 exhibited a ratio of 1.2 (Table 6.2). As the I_1/I_3 ratio was greater than 0.7, pyrene was again solubilized in the hydrocarbon chain region of the micelles. For both of these surfactant solutions, C_s was much greater than C_M , as previously determined (Table 5.2). For the solution of 0.10 % SDS / 0.90 % Triton X-100, C_s was approximately 60 times greater than C_M , 17.38 mM and 0.29 mM, respectively. For the solution of 1% Triton X-100, C_s was approximately 67 times greater than the CMC of

pure Triton X-100, 15.46 mM and 0.23 mM, respectively. Therefore, pyrene fluorescence again confirmed the presence of micelles in these solutions.

Table 6.2: Fluorescence Intensity of Pyrene in Solutions of Polymer, Surfactant and Polymer - Surfactant Complexes, 1.0% Polymer.

| POLYMERS | Ratio I_1 / I_3 |
|---|-------------------------------------|
| 1% Polyquaternium 10 | 1.7 |
| 1% MQNNED | 1.7 |
| 1% DQNNED | 1.7 |
| SURFACTANT | |
| 1% Triton X-100 | 1.2 |
| 0.10% SDS 0.90% Triton X-100 | 1.2 |
| POLYMER-SURFACTANT COMPLEXES | |
| 1% Polyquaternium 10 & 1% Triton X-100 | 1.3 |
| 1% MQNNED & 1% Triton X-100 | 1.3 |
| 1% DQNNED & 1% Triton X-100 | 1.3 |
| 1% Polyquaternium 10 & 0.10% SDS 0.90% Triton X-100 | 1.3 |
| 1% MQNNED & 0.10% SDS 0.90% Triton X-100 | 1.3 |
| 1% DQNNED & 0.10% SDS 0.90% Triton X-100 | 1.3 |

The similarity in fluorescence intensity of the two surfactant solutions again indicates that micelle composition has no effect on the I_1/I_3 ratio. It has been previously

reported ¹¹⁸ that the I_1/I_3 ratio is dependent upon the nature of the surfactant head group for pure surfactant solutions above the CMC ($I_1/I_3 = 1.1$ and 1.3 for SDS and Triton X-100, respectively). For mixed systems above the CMC of mixing, the I_1/I_3 ratio appears to reflect the nature of the surfactant mixture.

The single phase solutions containing 1% Polymer / 0.10% SDS / 0.90% Triton X-100 and 1% Polymer / 1% Triton X-100 were examined for the presence of polymer bound micelle clusters. Changes in pyrene fluorescence indicate that polymer bound micelle clusters are present in the polymer - surfactant systems (Table 6.2). This was determined from the decrease in the I_1/I_3 band which indicates the formation of hydrophobic domains in these complexes. The I_1/I_3 ratio observed of 1.3 is slightly higher than that of pyrene solubilized in free micelles. The similar values of I_1/I_3 for both surfactant solutions and polymer - surfactant complex solutions indicate that the polymer bound surfactant clusters and normal micelles have almost equal polarity when $C_s \gg C_M$. This result agrees with those of Nilsson for the system hydroxypropylmethylcellulose / SDS / water.^{121,122}

At surfactant concentrations greatly above the CMC either of mixing or of the pure surfactant, it is difficult to determine whether or not polymer bound micelle clusters exist without the use of fluorescence quenching or NMR. However, Winnik *et al.* and Nilsson ^{121,126} have presented evidence that, at high concentrations of surfactant, the bound surfactant clusters grow in size as more surfactant is added to the system. The results indicated that new clusters did not add to the polymer chain, but the polymer bound surfactant clusters were in competition with the formation of micelles.

Nilsson¹²¹ speculates that a pronounced difference exists between a very dilute polymer solution ($c < c^*$) and a concentrated solution ($c > c^*$). At low polymer concentrations, a constant number of binding sites was observed. Whereas, at high polymer concentration, the number of cluster binding sites increased. For dilute polymer solutions, viscosity measurements indicated that the association process was intramolecular.¹²¹ Whereas, for concentrated solutions, viscosity measurements indicated the association process was to be intermolecular as indicated by an increase in viscosity of the polymer - surfactant complex.¹²¹ In order to determine the type of interaction, we would need to determine the specific viscosity for our systems.

6.6 CONCLUSIONS

The I_1/I_3 ratio of the band intensities for pyrene with polymer alone indicate that pyrene is solubilized in a hydrophilic environment, possibly the solvation shell of the polymer molecules. This result is independent of polymer concentration.

At low and high surfactant concentration, 0.06% and 1%, the similarity in fluorescence intensity of the surfactant solutions indicates that micelle composition has no effect on the I_1/I_3 ratio. However, for mixed systems above the CMC of mixing, the I_1/I_3 ratio appears to reflect the nature of the surfactant mixture.

Changes in the vibronic fine structure of the pyrene fluorescence intensity spectra indicated that the micellar regions formed in the polymer-surfactant complexes were more hydrophilic than micelles formed in the absence of polymer. This result is independent of polymer concentration. At low concentrations of polymer ($c < c^*$) and surfactant ($C_s > C_M$), this result is consistent with the concept of smaller micelles being bound along the polymer strand. For smaller micelles, one would expect the water

penetration to be greater so that the pyrene would encounter more of the polar palisade layer of the micelle and the water associated with this layer. At high concentrations of polymer ($c > c^*$) and surfactant ($C_s \gg C_M$), the similar values of I_1/I_3 for both surfactant solutions and polymer - surfactant complex solutions indicate that the interiors of the polymer bound surfactant clusters and normal micelles have almost equal polarity.

CHAPTER 7

DYNAMIC LIGHT SCATTERING

7.1 INTRODUCTION

Dynamic light scattering (DLS) is an important tool in the study of polymer solutions for two reasons. First, DLS provides data on the molecular mobility and diffusion coefficients of polymers. Second, the data may be interpreted in terms of the size and configuration of the polymer.

DLS defines a wave vector, q ,

$$q = (4\pi n / \lambda_0) \sin(\theta / 2) \quad (7.1)$$

where λ_0 is the wave length of incident light in a vacuum, θ is the scattering angle and n is the refractive index of the medium. The full homodyne intensity autocorrelation function is measured as function of θ at 0° - 180° , caveat $\theta = 0^\circ$, with a correlator. The correlator samples the scattered light at controllably spaced periods in time to compute the time correlation function.¹³¹ In a dilute solution of a single, well dissolved polymer or micelle, measurement of the initial decay of the correlation function gives the mutual diffusion coefficient directly (Eq. 7.2).¹³²

$$\Gamma \equiv \frac{1}{2} \left\{ - \frac{d \ln [g^{(2)}(q, t) - 1]}{dt} \right\}_{t=0} = D_m q^2 \quad (7.2)$$

Usually, there is only one decay mode of the correlation function present (Figure 7.1). However, research groups have reported the observation of two and three decay modes of the correlation function in solutions containing either a polymer or a polymer and sodium dodecyl sulfate.¹³³⁻¹³⁵ These multiple modes may result from aggregation,¹³⁴ chain entanglement¹³⁵ or dynamic properties of the hydrophobic domains formed by uncharged segments of the polymer backbone.¹³³

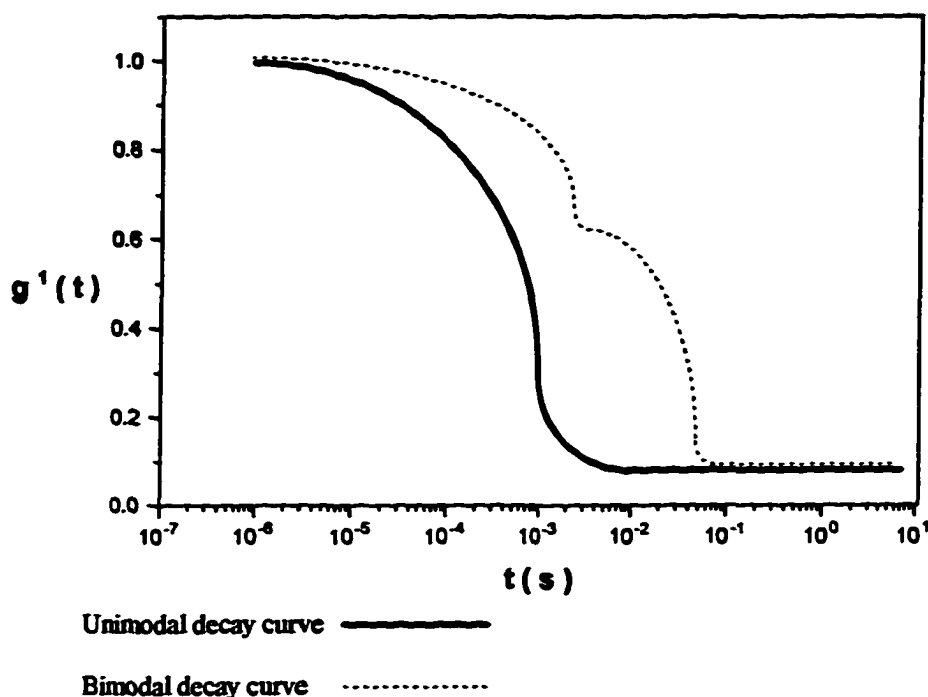


Figure 7.1 : Schematic Representation of Unimodal and Bimodal Decay Curves of the Correlation Function.

7.2 EXPERIMENTAL

7.2.1 Dynamic Light Scattering

Dynamic light scattering (DLS) measurements were made at scattering angles of 30-90° using a Lexel Model 95 Argon ion laser at 514.5 nm. During angle dependence studies, temperature was maintained at $25 \pm 0.05^\circ\text{C}$. Polymer and surfactant solutions were prepared as described in the fluorescence study and filtered with 0.2 μm Whatman PVDF filters to remove dust. Ionic strength of the solutions was adjusted to 0.10 M using a sodium chloride solution which was filtered with a 0.02 μm filter. This ionic strength was chosen to increase the scattering intensity and reduce intermolecular association of polymer - surfactant complexes. Addition of 0.1 M sodium chloride had

no effect on the clarity of the solutions. The samples were placed in silanated cells and centrifuged to remove any remaining dust particles. The sample cells were silanated by reacting the glass surface with chlorotrimethylsilane in hot toluene. Measurements were made in an index matching bath with toluene in order to minimize stray light and reflections. The full homodyne intensity autocorrelation function was measured at 30°, 45°, 60° and 90° with an ALV 5000 multiple- τ digital correlator. The correlation functions were recorded in real time “multiple- τ ” mode of the correlator in which 288 channels are logarithmically spaced over an interval from 0.2 μ s to approximately one hour.

7.2.2 Dynamic Light Scattering Data Analysis

Assuming the scattered field to have Gaussian statistics, the measured homodyne intensity autocorrelation function, $g^{(2)}(q,t)$, is directly related to the theoretical first order electric field autocorrelation function, $g^{(1)}(q,t)$, through the Siegert relation (Eq. 7.3):

$$g^{(2)}(q,t) = 1 + B(1 + f |g^{(1)}(q,t)|^2) \quad (7.3)$$

where $f (\leq 1)$ is an instrumental parameter and B is the baseline.

Since DLS measures the diffusion rate of particles in solution, the mutual diffusion coefficient can be obtained from a plot of the decay rate of $g^{(1)}(q,t)$ *versus* time using the following relationships:

$$g^{(1)}(q,t) = e^{-\Gamma t} \quad (7.4)$$

$$\Gamma = q^2 D_m \quad (7.5)$$

where Γ is the decay rate, q is the wave vector and D_m is the mutual diffusion coefficient.

The mutual diffusion coefficient is related to the hydrodynamic radius, R_h , by the Stokes-Einstein equation (Eq. 7.6):

$$D_m = k T / 6 \pi \eta R_h \quad (7.6)$$

where k is Boltzmann constant and η is the viscosity of the medium.

7.2.3 Cloud Point Determination

The cloud point of the solutions was determined visually using a waterbath that controlled the temperature from 25 to 70 ± 0.1 °C. Temperature was increased stepwise at a rate of 0.1 °C in 30 seconds.

7.3 RESULTS AND DISCUSSION

7.3.1 Cumulant Analysis

For experiments at 25°C, the correlation functions were nearly monoexponential at all angles for the Polyquaternium 10 polymer; the MQNNED and DQNNED polymers showing appreciable nonexponential character at low angles. The polymer - mixed surfactant micelle complexes exhibited more complex correlation functions with “tails” and “plateaus”. In all cases, a fourth order polynomial fit to the correlation functions was applied to extract Γ , the average decay rate, which, for the purposes of this chapter, corresponds to the main diffusive mode. As a reminder, the decay rate increases linearly with q^2 for purely translational diffusion of monodisperse particles. Deviations from linearity usually signal the presence of polydispersity and/or rotational motion of very large, asymmetric particles.

Figure 7.2 shows the dependence of Γ on q^2 for each polymer and polymer - mixed surfactant micelle complex. At a polymer concentration of 1 g/dL (c/c^* is 1.75,

2.00 and 4.00 for Polyquaternium 10, MQNNED and DQNNED, respectively), Γ scaled linearly with q^2 at all angles for the Polyquaternium 10 polymer, but an upward curvature was evident at high q for the MQNNED and DQNNED polymers. This effect was probably due to polydispersity. At high angles, the scattering form factor drops off for large molecules leaving the small molecules to dominate the scattering intensity and thus produce a positive sloping effect in the plot.

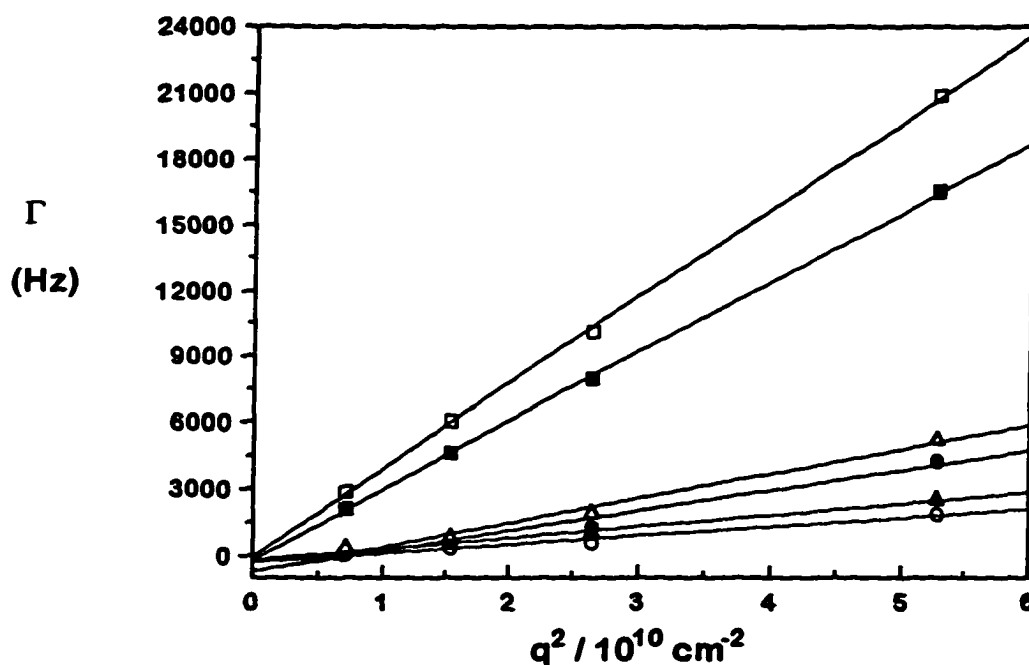


Figure 7.2 : Plot of Γ versus q^2 for Polymer and Polymer - Surfactant Complexes.
Symbols indicate: (■) 1% Polyquaternium 10; (□) 1% Polyquaternium 10 / 0.10% SDS / 0.90% Triton X-100; (●) 1% MQNNED; (○) 1% MQNNED / 0.10% SDS / 0.90% Triton X-100; (▲) 1% DQNNED ; and (Δ) 1% DQNNED / 0.10% SDS / 0.90% Triton X-100.

After addition of 0.10 SDS / 0.90% Triton X-100, the Polyquaternium 10 - mixed surfactant micelle complex formed was uniform as judged from the linearity of the plot. The data were replotted (Figure 7.3) to show the dependence of Γ/q^2 on q^2 . Table 7.1 displays values of $D_{m, app}$, the apparent mutual diffusion coefficient obtained from the intercepts of plots in Figure 7.3.

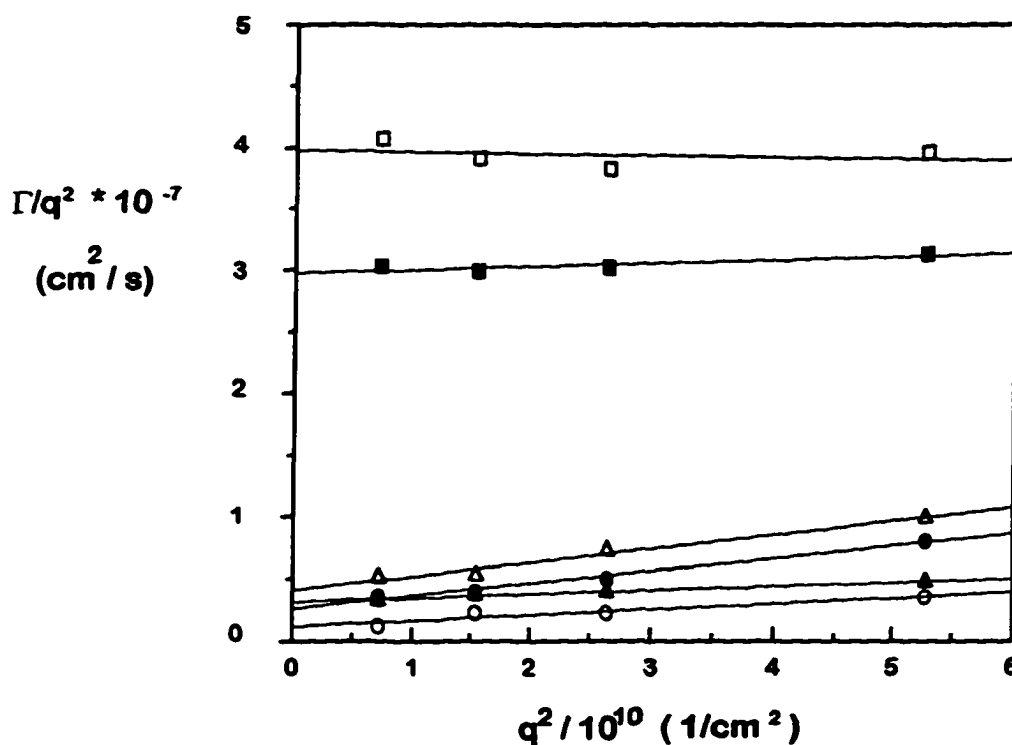


Figure 7.3 : Plot of the Apparent Mutual Diffusion Coefficient *versus* q^2 for Polymer and Polymer - Surfactant Complexes. Symbols indicate: (■) 1% Polyquaternium 10; (□) 1% Polyquaternium 10 / 0.10% SDS / 0.90% Triton X-100; (●) 1% MQNED; (○) 1% MQNED / 0.10% SDS / 0.90% Triton X-100; (▲) 1% DQNNED; and (△) 1% DQNNED / 0.10% SDS / 0.90% Triton X-100.

Table 7.1 - Effect of Surfactant Addition on $D_{m, app}$

| Polymer | $D_{m, app}$ 1% Polymer (cm^2/s) | $D_{m, app}$ 1% Polymer / 0.1% SDS / 0.9% Triton X-100 (cm^2/s) |
|----------------------|---|--|
| Polyquaternium 10 | $2.97 \cdot 10^{-7}$ | $3.98 \cdot 10^{-7}$ |
| MQNNED | $2.61 \cdot 10^{-8}$ | $1.13 \cdot 10^{-8}$ |
| DQNNED | $3.13 \cdot 10^{-8}$ | $3.94 \cdot 10^{-8}$ |

Table 7.2 - Scattering Intensity of Systems Studied

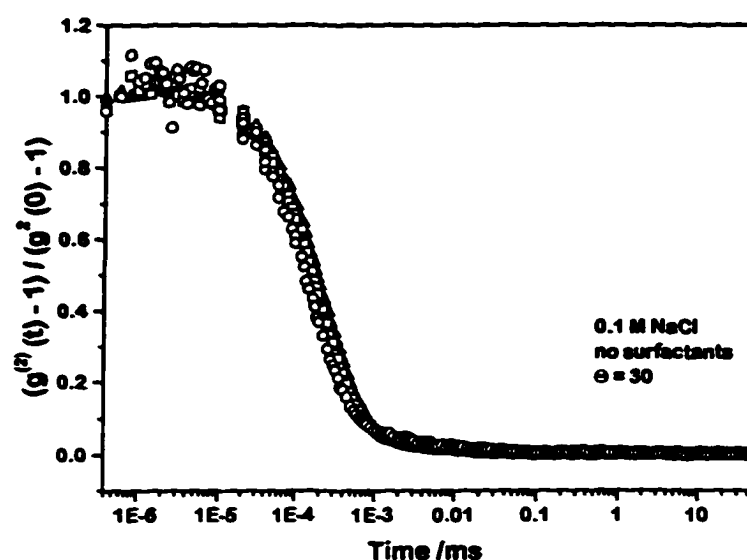
| System | Scattering Intensity (kHz) at $\theta = 90$ |
|---|---|
| Background (dark count) | 0.007 |
| 0.100 M NaCl solution | 0.014 |
| 0.1% SDS / 0.9% Triton X-100 in 0.100 M NaCl (mixed micelle) | 0.482 |
| 1% Polyquaternium 10 in 0.100 M NaCl | 1.749 |
| 1% Polyquaternium 10 and 0.1% SDS / 0.9% Triton X-100 in 0.100 M NaCl | 15.421 |
| 1% MQNNED in 0.100 M NaCl | 16.117 |
| 1% MQNNED and 0.1% SDS / 0.9% Triton X-100 in 0.100 M NaCl | 59.261 |
| 1% DQNNED in 0.100 M NaCl | 57.106 |
| 1% DQNNED and 0.1% SDS / 0.9% Triton X-100 in 0.100 M NaCl | 42.013 |

The value of $D_{m, app}$ increased after addition of the surfactant for both the Polyquaternium 10 and DQNNED polymers, the effect being more evident for the Polyquaternium 10 - mixed surfactant micelle system. The behavior of the MQNNED - mixed surfactant micelle complex was perplexing as the value of $D_{m, app}$ decreased by a factor of 2 after addition of surfactant implying an increase in the overall dimensions of the polymer - mixed surfactant micelle complex.

7.3.2 Temperature Dependence

The effect of temperature on the relaxation time of the polymers and the polymer-mixed surfactant micelle complexes was studied in the temperature range 25 - 40°C (Figures 7.4 - 7.6). The relaxation time of aqueous solutions of polymers was not greatly affected by temperature. However, the relaxation time of aqueous solutions of Polyquaternium 10 - mixed surfactant micelle complexes was affected when the temperature was increased to 40°C. This was indicated by both a bi-modal decay curve in plots of normalized $g^{(1)}(t)$ versus $\log_{10} t$ and a change in the solution from clear to turbid. The relaxation times of aqueous solutions of both MQNNED and DQNNED - mixed surfactant micelle complexes were not affected by increasing temperature to 40°C as indicated by unimodal decay curves for plots of $g^{(1)}(t)$ versus $\log_{10} t$ and a uniform increase in relaxation times. The results of the temperature study indicate that aqueous solutions of Polyquaternium 10 - mixed surfactant micelle complexes exhibit a different temperature response than polymer - mixed surfactant micelle complexes formed with polymers synthesized in our laboratories. The slow mode in the Polyquaternium 10 - mixed surfactant micelle complex at 40°C may originate from the formation of

(A)



(B)

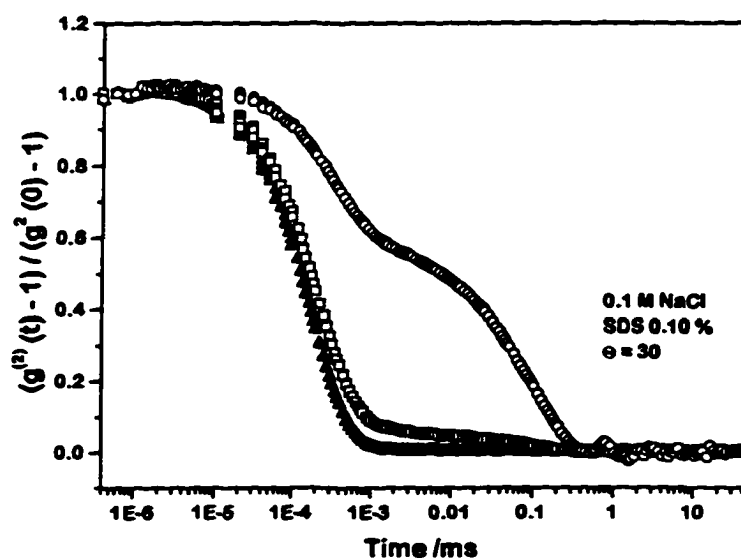
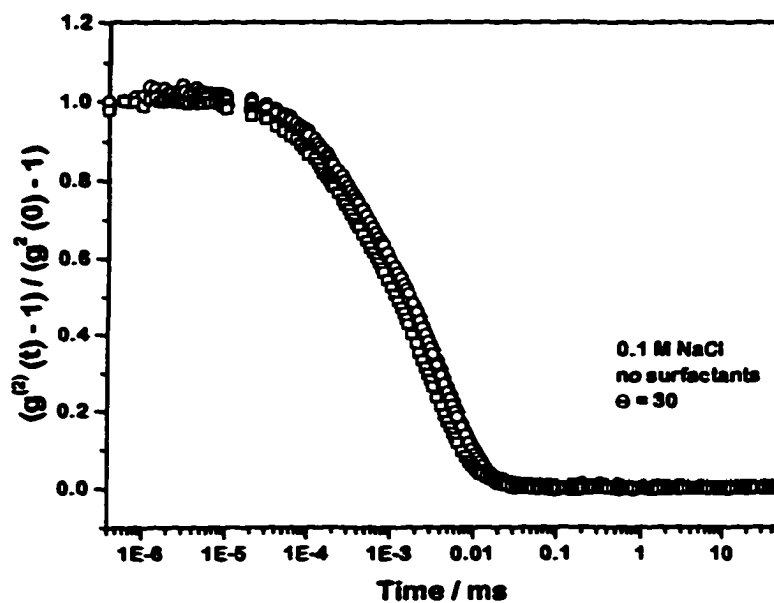


Figure 7.4 : Effect of Temperature on the Relaxation Rate of Polyquaternium 10 and Polyquaternium 10 - Mixed Micelle Complex: (A) aqueous solution of 1% Polyquaternium 10; (B) aqueous solution of 1% Polyquaternium 10 / 0.10% SDS / 0.90% Triton X-100; The symbols indicate \blacktriangle 25 °C; \square 30 °C; and \circ 40 °C.

(A)



(B)

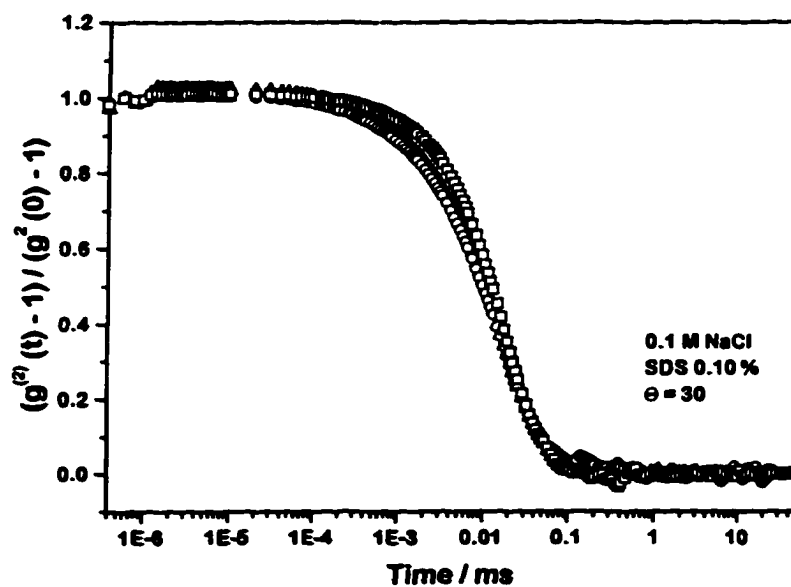
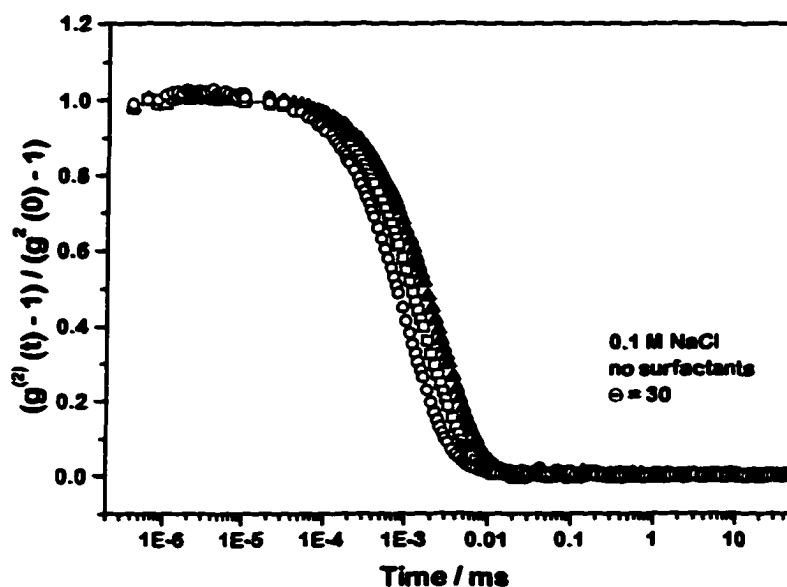


Figure 7.5 : Effect of Temperature on the Relaxation Rate of MQNNED and MQNNED - Mixed Micelle Complex: (A) aqueous solution of 1% MQNNED; (B) aqueous solution of 1% MQNNED / 0.10% SDS / 0.90% Triton X-100; The symbols indicate \blacktriangle 25 °C; \square 30 °C; and \circ 40 °C.

(A)



(B)

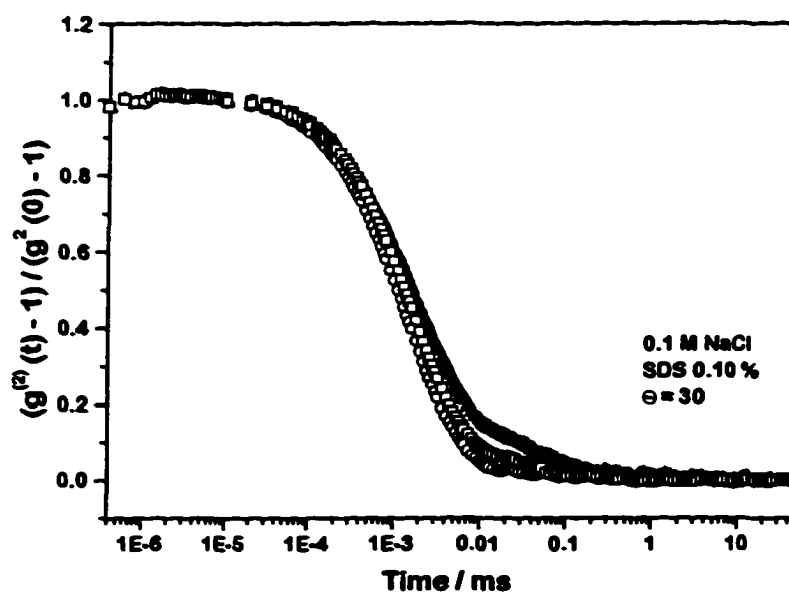


Figure 7.6 : Effect of Temperature on the Relaxation Rate of DQNNED and DQNNED - Mixed Micelle Complex: (A) aqueous solution of 1% DQNNED; (B) aqueous solution of 1% DQNNED / 0.10% SDS / 0.90% Triton X-100 The symbols indicate ▲ 25 °C; □ 30 °C; and ○ 40 °C.

polyelectrolyte clusters (aggregates) resulting from either attraction between the polyions or from entanglement of the polyelectrolyte chains.¹²² The change in the solution from clear to turbid, which is visible to the naked eye, is an indication of the formation of larger particles.

In order to determine the origin of the slow mode in the Polyquaternium 10 - mixed surfactant micelle complex, the cloud point temperature was investigated. The cloud point is defined as the temperature at which an aqueous nonionic surfactant solution becomes turbid.^{136,137} A change in the cloud point has been used to determine the effect of addition of electrolytes^{137,138} and ionic surfactants^{136,137,139} on solutions of nonionic surfactants. Valaulikar *et al.*¹³⁹ and Gu *et al.*¹³⁶ attribute the increase in the cloud point of Triton X-100 upon addition of small amounts of anionic surfactant to an increase in the surface charge density of the micelles. This interpretation implies that cloud point elevation is due to aggregation of the micelles as increased repulsion between micelles from addition of ionic surfactant makes it more difficult to cross the potential barrier.¹³⁶ Gu *et al.*¹³⁶ determined the cloud point of 1% Triton X-100 in the absence of both electrolyte and ionic surfactant to be 66.2 °C. It was shown that addition of 10^{-4} M (0.003%) SDS to a 1% solution of Triton X-100 increased the cloud point to approximately 77 °C. Further increases in the concentration of SDS caused the cloud point to increase asymptotically. These researchers went on to show that the addition of 0.01 M sodium chloride to this solution decreased the cloud point to approximately 68 °C.

The results of cloud point determination for the Polyquaternium 10 - mixed surfactant micelle complex used in the present study are given in Table 7.3. Despite the

fact that Gu et al.¹³⁶ reported no change in cloud point of 1% Triton X-100 when 0.01 M NaCl was added to the solution, we observed a decrease of 7.2 °C when 0.1 M NaCl was added to a 1% solution of Triton X-100. This decrease was eliminated when 0.1% ($3.5 \cdot 10^{-3}$ M) SDS was added to the system as the minimum possible cloud point was greater than 70 °C. The cloud point of the Polyquaternium 10 - mixed surfactant micelle complex was found to be lower than that of Triton X-100 alone by 16.4 °C. This result may indicate that the slow mode does not originate from the aggregation of the micelles, but rather from possible aggregation of the polymer - mixed surfactant micelle complexes. Polyquaternium 10 did not exhibit a cloud point in the temperature range studied. Therefore, the origin of the slow mode in the Polyquaternium 10 - mixed surfactant micelle complex may be attributed to aggregation of the polymer - surfactant complexes.

Table 7.3: Cloud Point Data

| Polyquaternium 10 (%) | SDS (%) | Triton X-100 (%) | NaCl (M) | Cloud Point (°C) | MPCP* (°C) |
|--------------------------------------|--------------------|-----------------------------|---------------------|-----------------------------|-----------------------|
| — | — | 1.0 | 0.1 | 59.0 | — |
| — | 0.1 | 0.9 | 0.1 | — | >70 |
| 1.0 | — | — | 0.1 | — | >70 |
| 1.0 | 0.1 | 0.9 | 0.1 | 42.6 | — |

* MPCP = minimum possible cloud point temperature

7.4 CONCLUSIONS

The results of cumulant analysis of the polymers and polymer - surfactant complexes indicated that both the Polyquaternium 10 and Polyquaternium 10 mixed surfactant micelle systems were effectively monodisperse. However, the systems of MQNED, DQNNED, MQNED mixed surfactant micelle and DQNNED mixed surfactant micelle complexes were polydisperse as determined from upward curvature in plots of the average decay rate *versus* q^2 at high q .

Temperature studies indicated that the aqueous solution of Polyquaternium 10 - mixed surfactant micelle complex exhibits a different temperature response than polymer - mixed surfactant micelle complexes formed with polymers synthesized in our laboratories. Therefore, polymer structure may play a role in aggregation phenomena of the polymer - mixed surfactant micelle complexes.

CHAPTER 8

SURFACE TENSION

8.1 INTRODUCTION

Surfactants and macromolecules (i.e. polymers and proteins) are widely used in the cosmetics and personal care industry. These components are used together in a variety of products, such as shampoos and hand lotions, to condition skin or hair. Their use is increasing as a variety of new 2 in 1 products (shampoos, bar soaps, sunscreens or hair colors) enter the market. Therefore, it is appropriate to study the interactions of these compounds.

8.2 INTERFACES

Every particle of matter possesses an interface at the boundary of its surroundings.^{67,81} An interface is defined as the boundary between two phases that exist together. There are two groups of interfaces: liquid interfaces and solid interfaces. In this work, we are interested to study the behavior of liquid interfaces. Liquid interfaces can be divided into three categories: gas/liquid, liquid/liquid and solid/liquid. The study of interfacial phenomena is relevant to the cosmetics, pharmaceutical and medical industry as the properties of the molecules at the interface are often different from those in the bulk of each phase. Interfacial phenomena affects the adsorption of drugs, penetration of molecules through biologic membranes such as the skin, emulsion formulation and stability, and human respiration.

8.3 SURFACE TENSION

Surface tension, the surface free energy per unit area, is the amount of work required to bring sufficient molecules to the surface from the interior of the liquid to expand it by unit area at a constant temperature.^{67,94,140} Molecules at the surface of the liquid have potential energies greater than those of similar molecules in the interior of the

liquid.⁹⁴ Therefore, an amount of work equal to the difference in the potential energy must be expended to bring a molecule from the interior of the liquid to the surface.^{94,140}

The interfacial tension, γ_i , for two pure liquids (Figure 8.1) is given by the following equation :

$$\gamma_i = \gamma_{aa} + \gamma_{bb} - 2\gamma_{ab} \quad (8.1)$$

and the interfacial free energy, E , is given by:

$$E = (A_{aa} - A_{ab}) + (A_{bb} - A_{ab}) = A_{aa} + A_{bb} - 2A_{ab} \quad (8.2)$$

If phase a is a gas then $\gamma_i = \gamma_b$ as molecules in the gas phase are far apart.⁹⁴

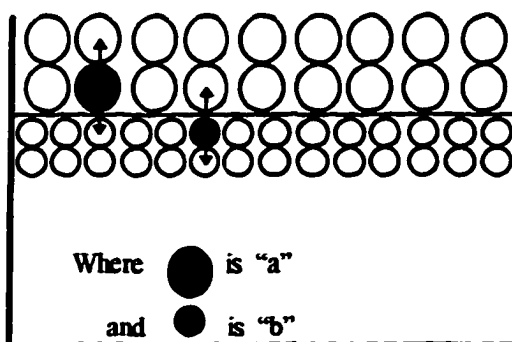


Figure 8.1: Interfacial Tension, γ_i , for Two Pure Liquids.

Certain molecules and ions when dispersed move of their own accord to the interface. The concentration at the interface then exceeds that in the bulk liquid. Therefore, the surface tension and surface free energy is reduced. This phenomenon is known as positive adsorption.^{67,140} Molecules and ions that are adsorbed at the interface are called surface active agents or surfactants.^{67,81} Depending on the structure of the molecule, the surfactant may be predominantly hydrophilic, lipophilic or balanced

between the two. The amphiphilic nature of surfactant monomers (molecules) causes them to be adsorbed preferentially at the interface.

Surfactant molecules, such as SDS, when added to water orient themselves with the hydrophilic head group in the water and the hydrophobic tail in the air (Figure 8.2). A consequence of this orientation is that some of the water molecules at the interface will be replaced by hydrocarbon or other nonpolar groups. Since the interaction force between water molecules and nonpolar groups is less than that between water molecules, adsorption of surfactants at the interface results in reduced surface tension of the solution. Since air consists of mainly nonpolar molecules, surface tension reduction by surfactants at the liquid/gas interface (L/G interface) occurs. Therefore, the presence in the surfactant molecule of a hydrophilic and hydrophobic moiety is a necessary condition for the reduction of surface tension. The efficacy of the surfactant varies with the nature of the solvent, temperature, electrolyte concentration, and amount of impurities or additives in the system.⁹⁴

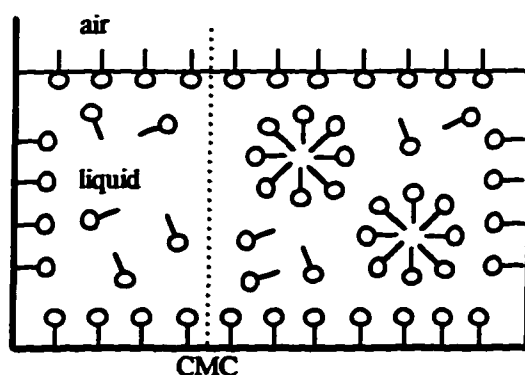


Figure 8.2: Orientation of Surfactant Monomers in Water.

Surface tension plots for surfactant solutions exhibit a significant decrease with concentration initially, followed by a sharp break above which the surface tension remains essentially constant. The break is due to the formation of surfactant clusters (micelles) and the break point is called the critical micelle concentration (CMC). Above this concentration, almost all of the added surfactant monomers are consumed in micelle formation and the monomer concentration does not increase appreciably. Therefore, the surface tension remains essentially constant above the CMC and can be related directly to the activity of the monomeric species in solution.

Any solute which has a positive adsorption at the interface will decrease the surface tension. Similarly, a component which has a negative surface excess can actually lead to an increase in surface tension of the solvent. Since the changes in surface tension can be related to the activity of the monomeric surfactant species in solution, interactions of surfactant with other species which result in changes of monomer activity can be monitored.

8.4 THE WILHELMY PLATE METHOD

Many methods have been developed to determine surface tension of solutions, such as Wilhelmy plate, DuNouy ring, capillary rise, drop-weight, maximum bubble pressure, and sessile drop method. The Wilhelmy plate method, named after Ludwig Wilhelmy ¹⁴¹, is a simple method to determine static (advancing and receding) and dynamic contact angles. When a liquid comes into contact with a solid surface, if sufficient tension exists then the liquid will wet the solid. The equilibrium condition for wetting of a solid surface by a liquid is a three phase equilibrium of liquid, solid and vapor ¹⁴² (Figure 8.3). The intersection of the solid-liquid, liquid-vapor and solid-vapor

interfaces is the equilibrium contact point. A force balance acts on this intersection and represents the surface tension. The balance equation for the contact angle, Θ , was determined by Young and Dupre¹⁴².

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta \quad (8.3)$$

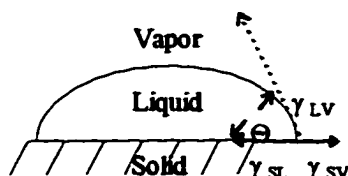


Figure 8.3: Drop of Liquid Wetting a Solid Surface.

The same concept holds true for a vertical solid surface contacting a liquid in a trough (Figure 8.4).

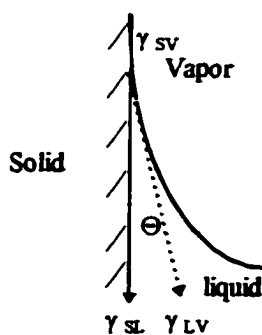


Figure 8.4: Drop of Liquid Wetting a Vertical Solid Surface.

The Wilhelmy plate method uses a force balance on a platinum plate of known dimensions which enters vertically into the wetting liquid (Figure 8.5)

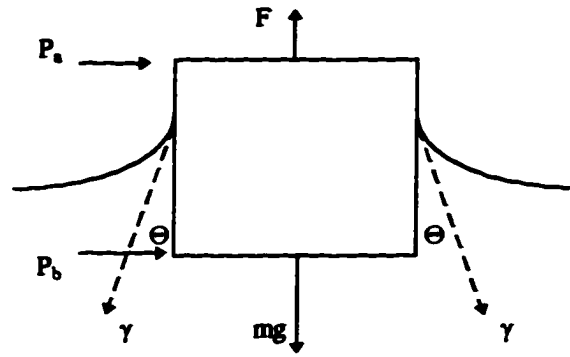


Figure 8.5: Wilhelmy Plate and Forces Acting upon it.

The equation to balance the forces acting upon the plate is given as:

$$F - mg - P \gamma \cos \Theta + A(P_a - P_b) = 0 \quad (8.5)$$

where F is the upward force holding the plate in a stationary position, m is the mass of the plate, g is gravitational force, P is the perimeter of the plate (the wetting length), γ is the surface tension, Θ is the contact angle, A is the cross sectional area of the plate, P_a and P_b are the hydrostatic pressure at the top and bottom of the plate, respectively.

Therefore, $A(P_a - P_b)$ is the buoyancy term.

Combining the terms of Eq. 8.5 yields:

$$F - mg + A(P_a - P_b) = F_{\text{wilhelmy}} = P \gamma \cos \Theta \quad (8.6)$$

$$\gamma = F_{\text{wilhelmy}} / P \cos \Theta \quad (8.7)$$

where F_{wilhelmy} is the Wilhelmy force or measured force.

If the liquid is spread on to a roughened platinum plate, which is a high energy metallic surface, the contact angle may be assumed to be zero. Therefore, $\cos \Theta = 1$ and

Eq. 8.7 becomes:

$$\gamma = F_{\text{wilhelmy}} / P \quad (8.8)$$

8.5 SURFACE TENSION OF SURFACTANT SOLUTIONS

8.5.1 Surfactant Efficiency

Surfactant efficiency is defined as the bulk phase concentration of surfactant required to reduce the surface tension of a solution by some significant amount.⁹⁴ Efficiency is measured as the - logarithm of the bulk phase concentration of surfactant necessary to produce a decrease in surface tension of 20 mN / m. Reduction of surface tension depends upon the replacement of solvent molecules at the interface by surfactant molecules. Therefore, efficiency reflects the concentration of surfactant at the interface relative to that in the bulk solution.⁹⁴ Efficiency can be determined by the ratio of the concentration of surfactant at the interface, C_1 , *versus* the concentration in the bulk solution, C_2 .

$$\text{Efficiency} = C_1 / C_2 \quad (8.9)$$

The relationship between C_1 and C_2 is:

$$C_1 = (1000 \Gamma / d) + C_2 \quad (8.10)$$

where d is the thickness of the interfacial region in cm and Γ is the surface excess concentration in moles/cm².⁹⁴ Therefore, Eq. 8.10 becomes:

$$C_1 / C_2 = (1000 \Gamma / d C_2) + 1 \quad (8.11)$$

When surface tension is reduced by 20 mN / m, the value of Γ is close to the minimum value and most of the surfactant molecules are tilted to the interface.⁹⁴

Assuming that the thickness of the interfacial region, d , is inversely proportional to the surface area per adsorbed molecule, a_2 , then Γ / d may be considered to be constant.⁹⁴ Therefore, $C_1 / C_2 = (K_1 / C_2) + 1$ where K_1 is a constant. Therefore,

the bulk concentration of surfactant necessary to decrease the surface tension by 20 mN/m is a measure of efficiency.

Since $C_1 / C_2 = \exp (-\Delta G / R T)$ where ΔG is the free energy of transfer of a surfactant molecule from the bulk of the liquid to the interface, at $\Pi = 20$ dynes / cm, this relationship may be expressed as:

$$\log C_1 / C_2 = \log (K_1 / C_2)_{\Pi=20} = (-\Delta G_{TR} / 2.303 R T) \quad (8.12)$$

where ΔG_{TR} is the free energy of transfer from the interior of the liquid to the interface at $\Pi = 20$.

For an ionic surfactant in aqueous solution, efficiency increases as the length of the hydrocarbon chain is increased.⁹⁴ Efficiency is increased by addition of a phenyl group to the hydrocarbon chain, increasing the binding of the surfactant counterion and the addition of water structure promoters such as xylose and fructose. Branching in the hydrocarbon chain of the surfactant and addition of water structure breakers such as N-methylacetamide decreases efficiency.⁹⁴

8.5.2 Surfactant Effectiveness

Surfactant effectiveness is defined as the maximum reduction in surface tension that can be obtained regardless of the bulk phase concentration of surfactant.⁹⁴ Effectiveness can be measured by the amount of reduction obtained at the CMC, Γ_{CMC} , since reduction of surface tension beyond the CMC is relatively insignificant.

The Krafft point, T_K , is the temperature at which the solubility of an ionic surfactant becomes equal to the CMC.⁹⁴ The Krafft point for SDS is 16°C.¹⁴³ Above the Krafft point, maximal reduction of surface tension occurs at the CMC of the surfactant.

At concentrations below but near the CMC, the interface becomes saturated with surfactant monomer.

Surfactant effectiveness is dependent upon the surface concentration of the surfactant at saturation adsorption, the logarithm of the CMC, and the logarithm of the efficiency factor $(\log (1 / C_2))_{\Pi-20}$.⁹⁴ The larger the surface concentration attained by the surfactant, the higher its CMC and the lower its bulk concentration required to decrease the surface tension by 20 mN / m, the greater the reduction of surface tension at the CMC.

Effectiveness of ionic surfactants is increased slightly by increasing the hydrocarbon chain length and increasing adsorption at the L/G interface via replacement of an inorganic surfactant counterion with a straight chain, surface active counterion such as $C_{10}H_{21}N(CH_3)_3^+$.⁹⁴ Mutual neutralization of charge in the ion pair results in close packing at the interface and an unusually high effectiveness for reducing surface tension.⁹⁴ Compounds of this type are formed when long chain amines are added to anionic detergents for foam stabilization properties. The addition of neutral electrolyte to an aqueous solution of ionic surfactant increases effectiveness due to compression of the electrical double layer. Compression of the electrical double layer decreases the repulsion between ionic head groups on the surfactant monomers and results in closer packing at the L/G interface.⁹⁴

8.6 SURFACE TENSION OF MULTI-COMPONENT SYSTEMS

8.6.1 Uncharged Polymer and Sodium Dodecyl Sulfate

The properties of solutions containing both a polymer and a surfactant have been explained by assuming the formation of a polymer-surfactant complex resulting from the

binding of the surfactant ions onto the polymer chain.¹⁴⁴ In the case of an uncharged polymer and charged surfactant, hydrophobic bonding is the main force responsible for the interaction. Jones¹⁴⁴ was one of the first investigators to study the interaction of an uncharged, weakly surface active polymer and SDS by surface tension. He studied a system of polyethylene oxide, a water soluble polymer with no side group, and increasing amounts of SDS. Other studies used polyvinyl alcohol and polyvinylpyrrolidone which have polar side groups.¹⁴⁵⁻¹⁴⁷

The surface tension plots of the mixed system were different from that of pure SDS. Two critical surfactant concentrations were noted (Figure 8.6). T_1 is the concentration of SDS at which interaction first occurs. T_2' is the concentration of SDS at which the polymer becomes saturated with surfactant. After the sites on the polymer are saturated, the SDS monomer concentration will increase until micelles are formed at T_2 .⁹³

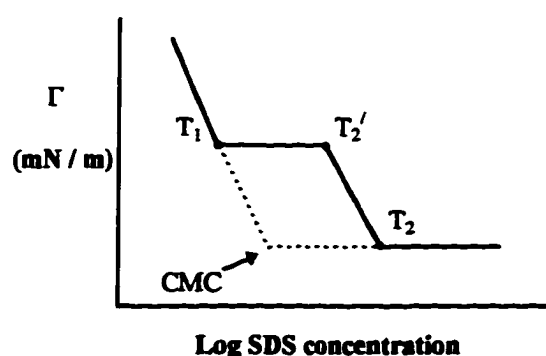


Figure 8.6: Surface Tension Plot for System of Uncharged Polymer and Anionic Surfactant.

From the results of this study, the assumption was made that surface tension is a sensor of the free surfactant concentration in solution, and the surface activity of the

surfactant monomer exceeds that of the polymer surfactant complex.^{144,148} Therefore, surface tension can be used as a method to monitor the concentration changes of uncomplexed surfactant in mixed systems.

Since T_1 occurs at a surfactant concentration less than the CMC of SDS, one can deduce that the polymer - surfactant complex state is a more favorable energy condition for SDS monomer than regular micelles.⁹³ T_1 is weakly dependent upon polymer concentration¹⁴⁴; whereas, T_2' , which corresponds to the saturation of the polymer with SDS monomer, is directly proportional to the polymer concentration.¹⁴⁸

Jones¹⁴⁴ concluded that the two transition points separate a region of no interaction between polymer and SDS, a region of approximately stoichiometric interaction of the species, and a region in which micelles begin to be formed.

The essential features of these surface tension plots of uncharged polymer and charged surfactant are: 1.) T_1 is weakly dependent upon polymer concentration except at low concentrations of polymer¹⁴⁴; 2.) T_2' is directly proportional to the polymer concentration¹⁴⁸; 3.) the addition of salt decreases T_1 and its variation with polymer concentration; therefore association occurs at lower concentrations of surfactant⁹³; and 4.) the initial constant surface tension, which implies constant SDS activity, is evident at increasing polymer concentrations.¹⁴⁹ If the polymer is surface active, the results are said to be more difficult to interpret.⁹³

8.6.2 Charged Polymer and Sodium Dodecyl Sulfate

Goddard and coworkers^{52,85,89,93,101} have studied the interaction of Polyquaternium 10 (i.e. JR400) with SDS using surface tension. Polyquaternium 10 is a quaternized hydroxyethyl cellulose derivative with the quaternary nitrogen located at the

end of a flexible ethylene oxide graft.⁵⁰ From these surface tension studies, it was determined that a cationic polymer and SDS produced a similar interaction zone as an uncharged polymer and SDS. However, the interaction zone was shifted to much lower surfactant concentrations for the cationic polymer and SDS than for uncharged polymers and SDS⁸⁹ (Figure 8.7). From these studies, no interaction was detected between the parent polymer, hydroxyethyl cellulose, and SDS by surface tension method.^{85,89,93,101,150}

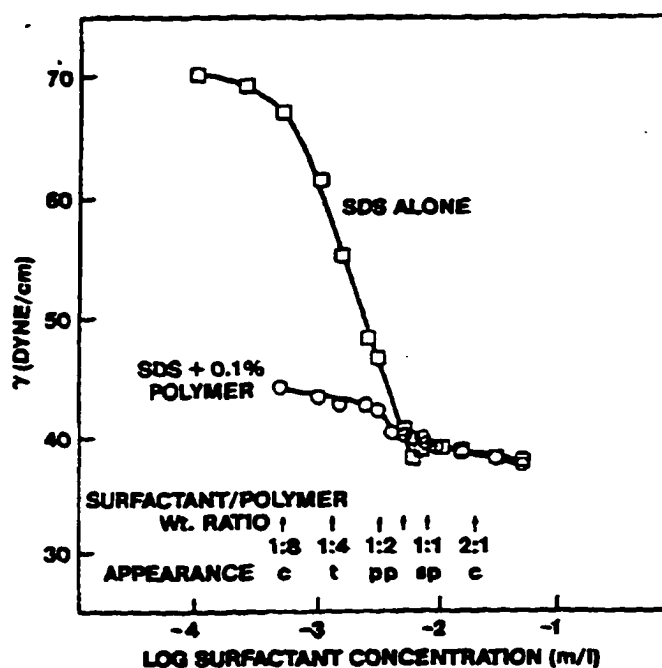


Figure 8.7: Surface Tension/Concentration Curves of SDS with and without Polymer JR400. The terms c, t, p, and sp refer to clear, turbid, precipitate, and slight precipitate, respectively. (Reproduced from Goddard, E. D. *et al.*, *J. Soc. Cosmet. Chem.*, 26, 461, 1975. With permission.)

The essential features of the surface tension plots of cationic Polyquaternium 10 and SDS are: 1.) a synergistic lowering of the surface tension at very low concentrations of SDS which implies the formation of a highly surface active polymer - surfactant complex; 2.) the persistence of a low surface tension even in the zone of high

precipitation; and 3.) coincidence with the surface tension curve of SDS solution in the micellar region.^{85,93} Goddard and coworkers⁹³ have explained these phenomena as the result of changes in surface active species present at the interface due to the progressive uptake of the SDS by the polymer (Figure 8.8).

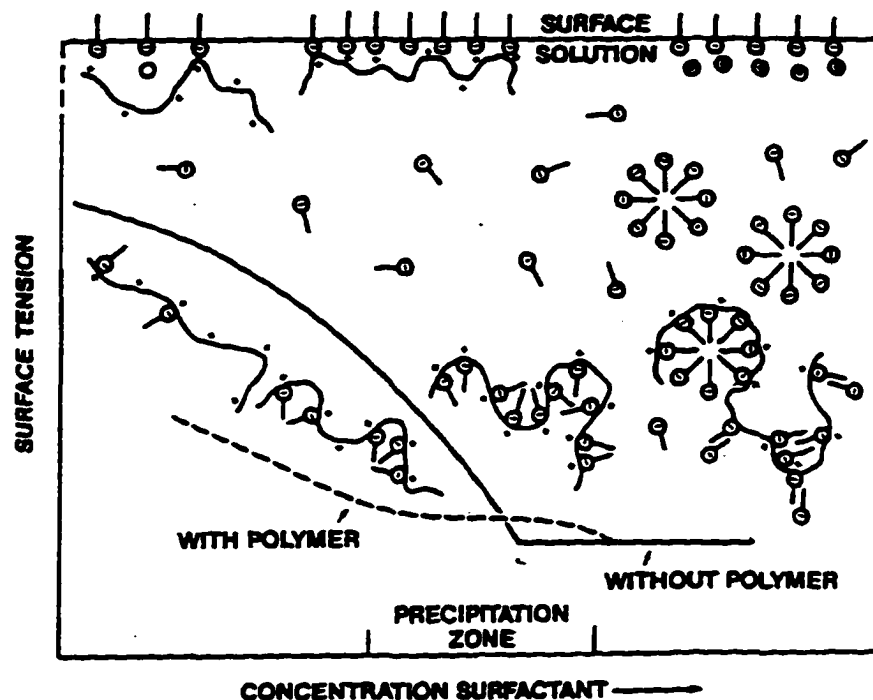


Figure 8.8: Conditions in the Bulk and Surface of a Solution Containing a Polycation (Fixed Concentration) and Anionic Surfactant. Full line is the hypothetical surface tension/concentration curve of the surfactant alone; dotted line is that of the mixture with the polycation. Simple counterions are depicted only in the surface zone. (Reproduced from Goddard, E. D., Polymer - surfactant interaction. Part II. Polymer and surfactant of opposite charge., In: Interactions of Surfactants with Polymers and Proteins, CRC Press, Boca Raton, 1993. With permission.)

This study of surface tension was extended to include various vinyl polycations.⁹⁰

The results indicated that cationic charge centers located along the backbone give much lower surface tension values in the precipitation zone than other quaternary derivatives.

Also, if the charge density was high, the precipitated material could not be resolubilized. In all cases, the presence of the polymer, which is itself weakly surface active, produced a sharp decrease in surface tension at SDS concentrations below the CMC.⁹⁰ Adsorption of SDS decreased the solubility of the polymer and made it highly surface active at the L/G interface thereby producing a decrease in surface tension greater than that of SDS alone. Resolubilization of the complex caused the surface tension to coincide with that of SDS alone beyond the CMC. These studies imply that the formation of a highly surface active macromolecular species with outwardly extended alkyl groups is responsible for surface activity in the precipitation region as represented (Figure 8.8).⁹³ An increase in foaming power of these solutions, which is a direct consequence of the increased surface activity of the Polyquaternium 10 - SDS complex formed, was also observed.⁵²

8.7 EXPERIMENTAL

Solutions were prepared by addition of a concentrated polymer solution (1-3%) to a solution of SDS. The solutions were stirred and allowed to equilibrate overnight. Surface tension measurements were obtained with a Kruss K14 tensiometer using the Wilhelmy plate method at 20 ± 0.5 °C. The tensiometer was calibrated with distilled, deionized water. The platinum plate was cleaned prior to use and between each measurement by flaming the surface in a propane flame to remove surface deposits. All surface tension measurements were made in triplicate and error bars are based upon these measurements.

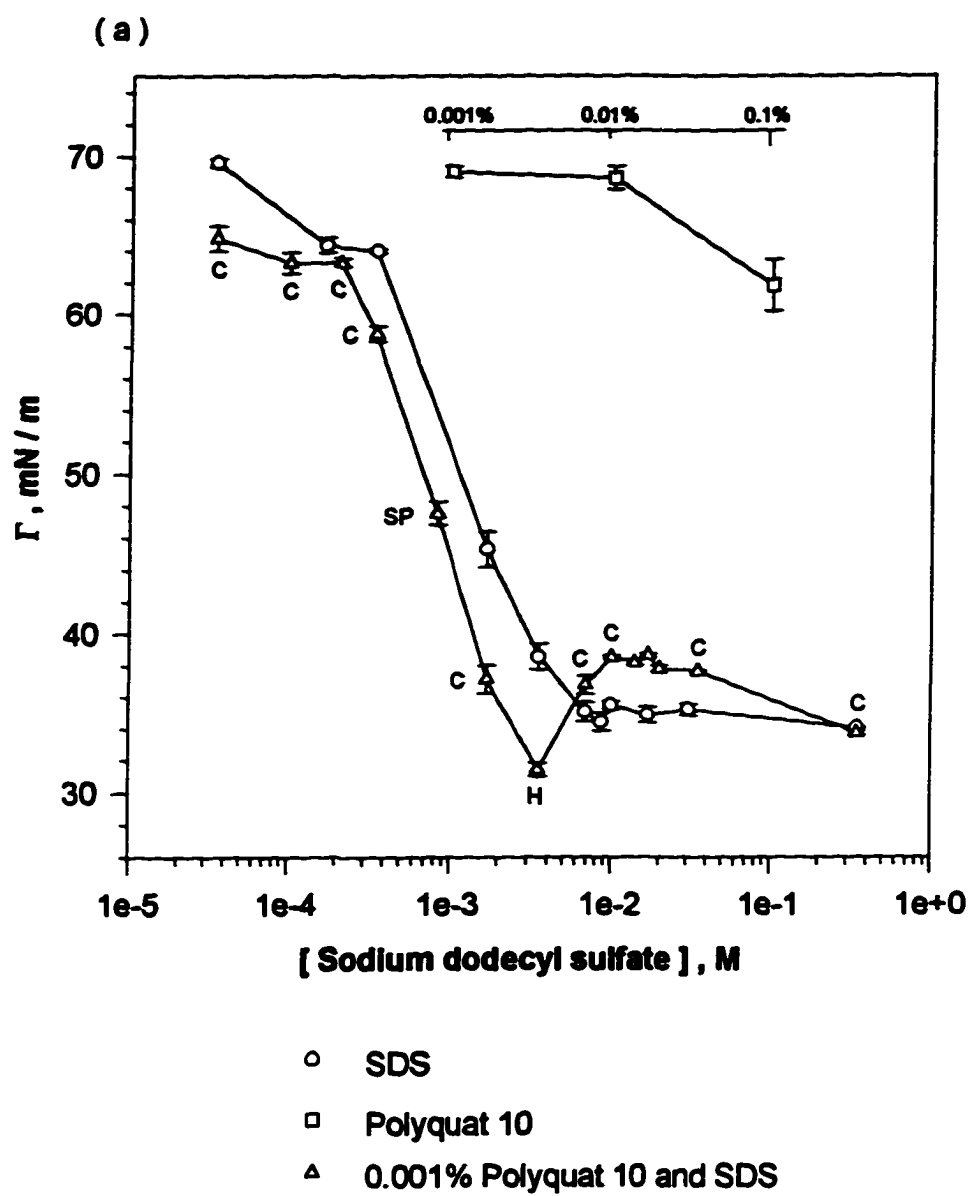
8.8 RESULTS AND DISCUSSION

8.8.1 Effect of Polymer - Sodium Dodecyl Sulfate Complex on Surface Tension

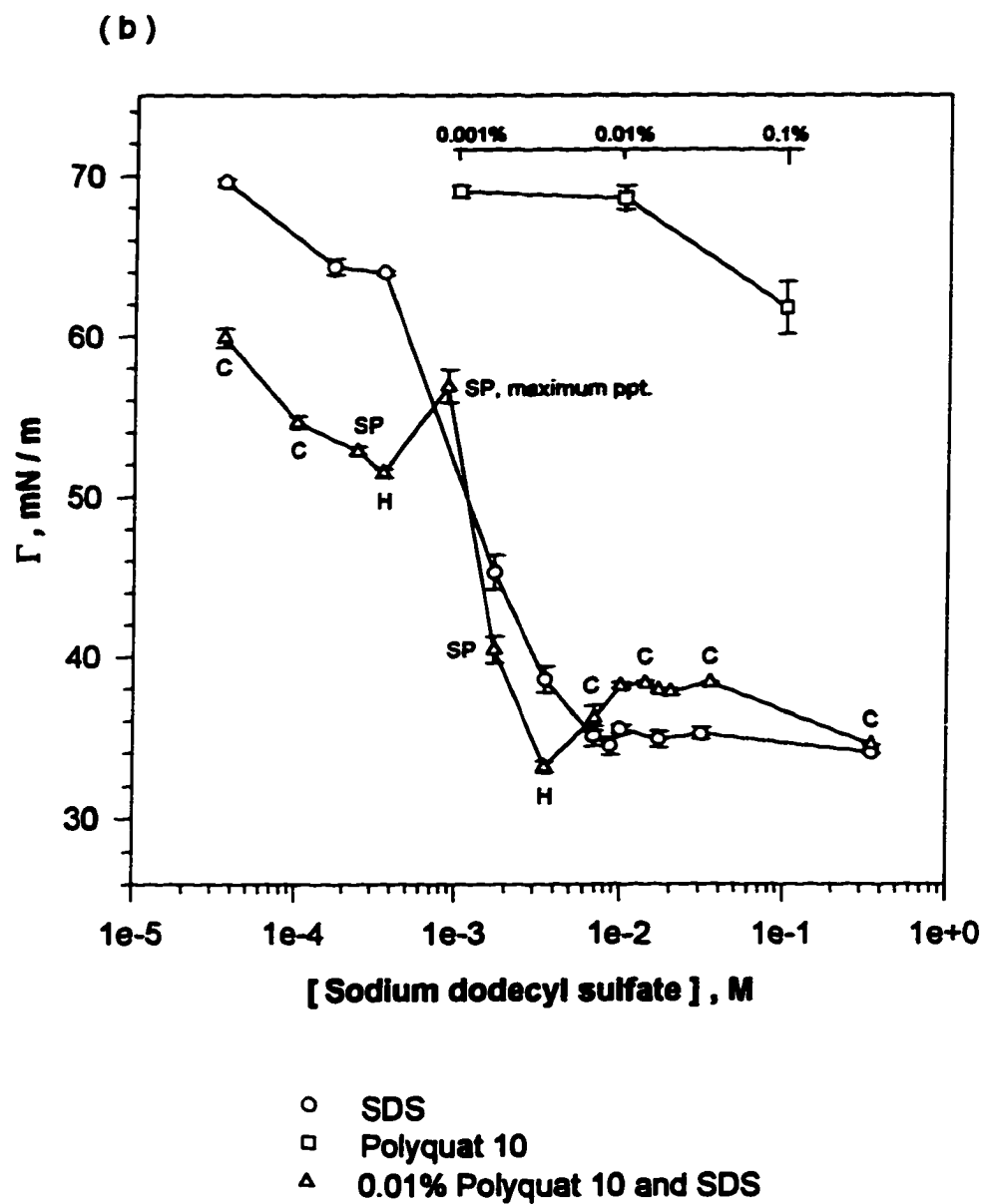
A plot of surface tension *versus* surfactant concentration exhibits a significant decrease with increasing concentration initially, followed by a plateau where the surface tension remains essentially constant. The plateau is due to the formation of surfactant clusters (micelles) and the break point is called the critical micelle concentration (CMC). Above this concentration, almost all of the added surfactant monomers are consumed in micelle formation and the monomer concentration does not increase appreciably. Therefore the surface tension remains essentially constant above the CMC and can be related directly to the activity of the monomers in solution. Any solute which has a positive adsorption at the interface will decrease the surface tension. Similarly, a component which has a negative surface excess can actually lead to an increase in surface tension of the solvent. Since the changes in surface tension can be related to the activity of the monomeric surfactant species in solution, interactions of surfactant with other species which result in changes of monomer activity can be monitored.

Using the Wilhelmy plate method, surface tension was studied as a function of surfactant concentration at fixed concentrations of polymer. The results for the interaction of Polyquaternium 10 and SDS are given in Figure 8.9. The polymer by itself is only slightly surface active at the air/water interface. The reduction in surface tension by a 0.1% Polyquaternium 10 solution is approximately 8 mN / m greater than that of a 3.5×10^{-5} M (0.001%) solution of SDS. This result agrees with a previously published result by Goddard and Hannan.⁵²

Figure 8.9: Surface Tension of Polyquaternium 10 - SDS Complexes.
(a) 0.001% Polyquaternium 10 and SDS
(b) 0.01% Polyquaternium 10 and SDS
(c) 0.1% Polyquaternium 10 and SDS
Symbols indicate: C = clear solution, H = hazy solution,
SP = slight precipitate, and P = precipitate.

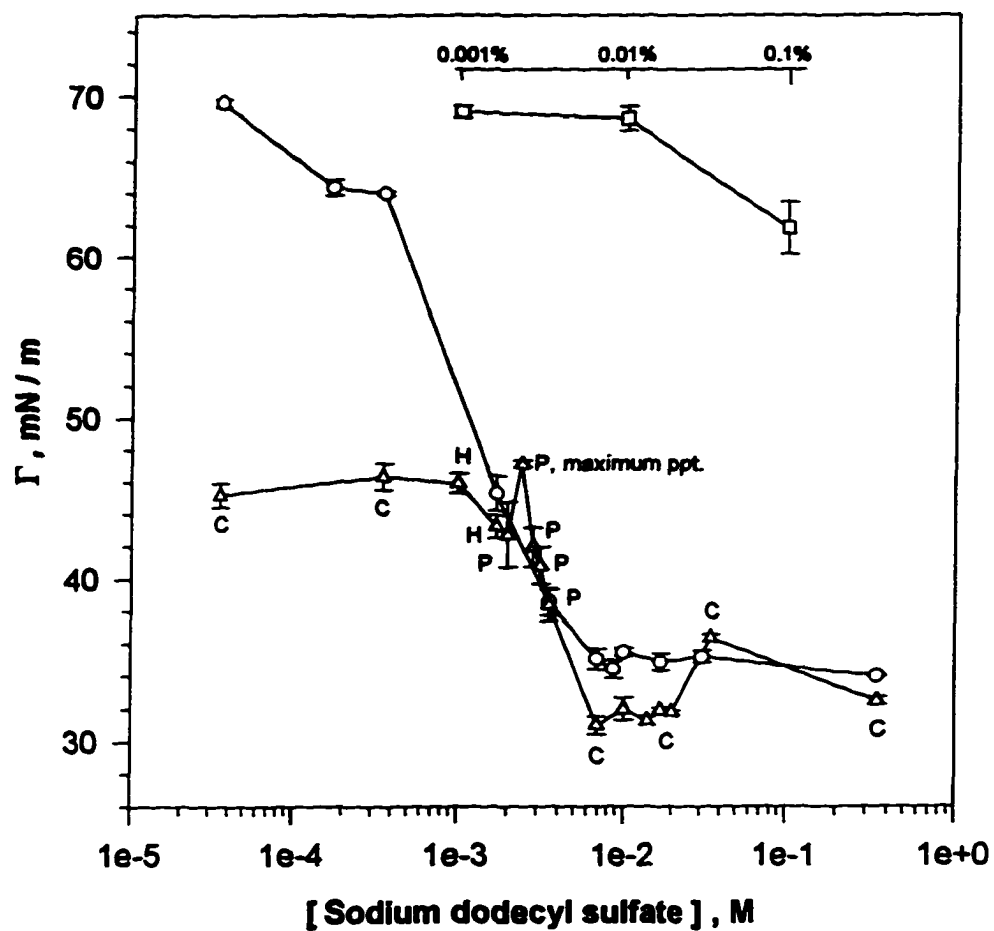


(Figure continued)



(Figure continued)

(c)



- SDS
- Polyquat 10
- △ 0.1% Polyquat 10 and SDS

The complex formed by association of the negatively charged SDS monomers with the cationic polymer is highly surface active (Figure 8.9) as shown by the reduction of surface tension. This effect is especially pronounced at low concentrations of surfactant and high levels of polymer. A solution comprised of 0.1% Polyquaternium 10 and $3.5 \cdot 10^{-5}$ M SDS reduced surface tension of water to the same extent as a $1.7 \cdot 10^{-3}$ M SDS solution. This reduction in surface tension continues despite precipitation of the polymer surfactant complex and coincides with the curve for SDS as the complex is resolubilized at higher SDS concentrations where micelle formation occurs. This lowering of the surface tension has been attributed to modification of the polymer by adsorption of SDS anions at the cationic sites (Figure 8.8).⁵² However, any synergistic effect is difficult to describe as the slope of the surface tension plots in the presence of polymer is governed by the free SDS monomer concentration, the activity of the polymer - surfactant complex and the amount of precipitate formed.

Surfactant efficiency, the concentration of SDS necessary to reduce the surface tension by 20 mN / m,⁹⁴ is $1.7 \cdot 10^{-3}$ M for solutions of SDS in water. In contrast, the efficiency of the 0.1% Polyquaternium 10 - SDS complex occurred at a surfactant concentration of $3.5 \cdot 10^{-5}$ M. Therefore, the complex is approximately 50 times more efficient in reducing surface tension than the surfactant alone. Surfactant effectiveness is defined as the maximum reduction in surface tension that can be obtained regardless of the bulk phase concentration of the surfactant.⁹⁴ Effectiveness is measured by the amount of reduction in surface tension obtained at the CMC of the surfactant since reduction of surface tension beyond the CMC is relatively insignificant. Effectiveness for the polymer - surfactant complex is defined as the maximum reduction in surface tension

that can be obtained regardless of the bulk phase concentration of the polymer and surfactant. Polymer - surfactant complex effectiveness is measured by the amount of reduction in surface tension obtained by the complex at the CMC of the surfactant. The complex of 0.1% Polyquaternium 10 and SDS is more effective at reducing surface tension than SDS alone; whereas, solutions containing 0.001 and 0.01% Polyquaternium 10 and SDS are slightly less effective at reducing surface tension than SDS alone.

In a similar manner (Figure 8.10), complexation of SDS with a slightly surface active monoquaternary polymer (MQNNED) derived from carboxymethyl cellulose was studied. Large decreases in surface tension at low concentration of SDS were observed. This effect also remained in the presence of precipitated complex, and the curve eventually coincided with the surface tension curve for SDS as resolubilization of the complex occurred. Increasing the polymer concentration also produced greater decreases in surface tension. The solution that produced the most efficient decrease in surface tension as compared to SDS was 0.1% MQNNED - $3.5 \cdot 10^{-5}$ M SDS. A solution of 0.1% MQNNED - SDS was more effective at reducing surface tension than SDS alone. Solutions of 0.001 and 0.01% MQNNED and SDS were slightly less effective at reducing surface tension than SDS alone.

Finally, the effect of complexation of SDS with a slightly surface active diquaternary polymer (DQNNED) on surface tension was studied. Initially, at low concentrations of surfactant and 0.1% polymer, surface tension decreased markedly relative to the surface tension of the SDS solutions (Figure 8.11). Again, the most efficient polymer - surfactant system observed contained 0.1% DQNNED and $3.5 \cdot 10^{-5}$ M SDS.

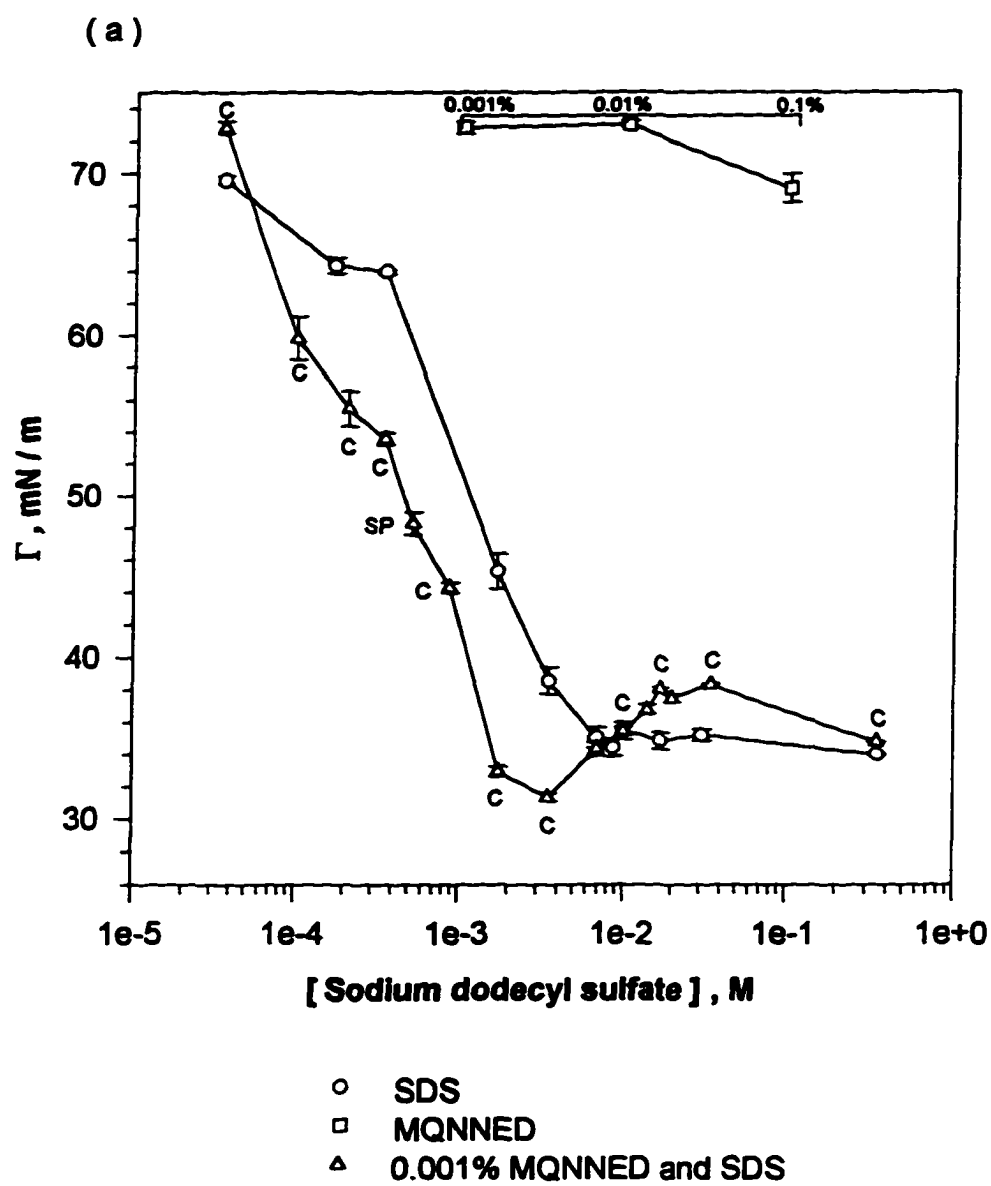
Figure 8.10: Surface Tension of MQNNED - SDS Complexes.

(a) 0.001% MQNNED and SDS

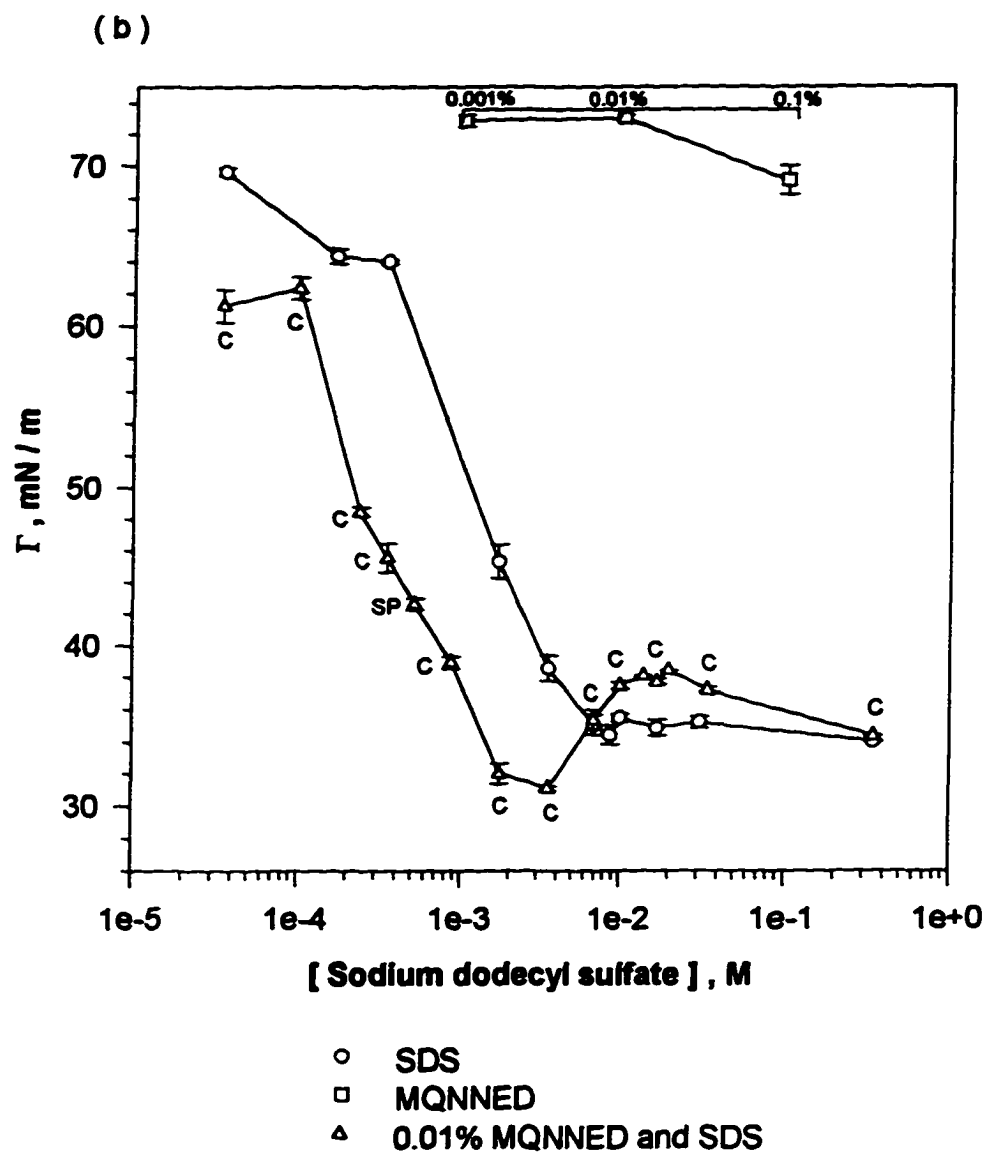
(b) 0.01% MQNNED and SDS

(c) 0.1% MQNNED and SDS

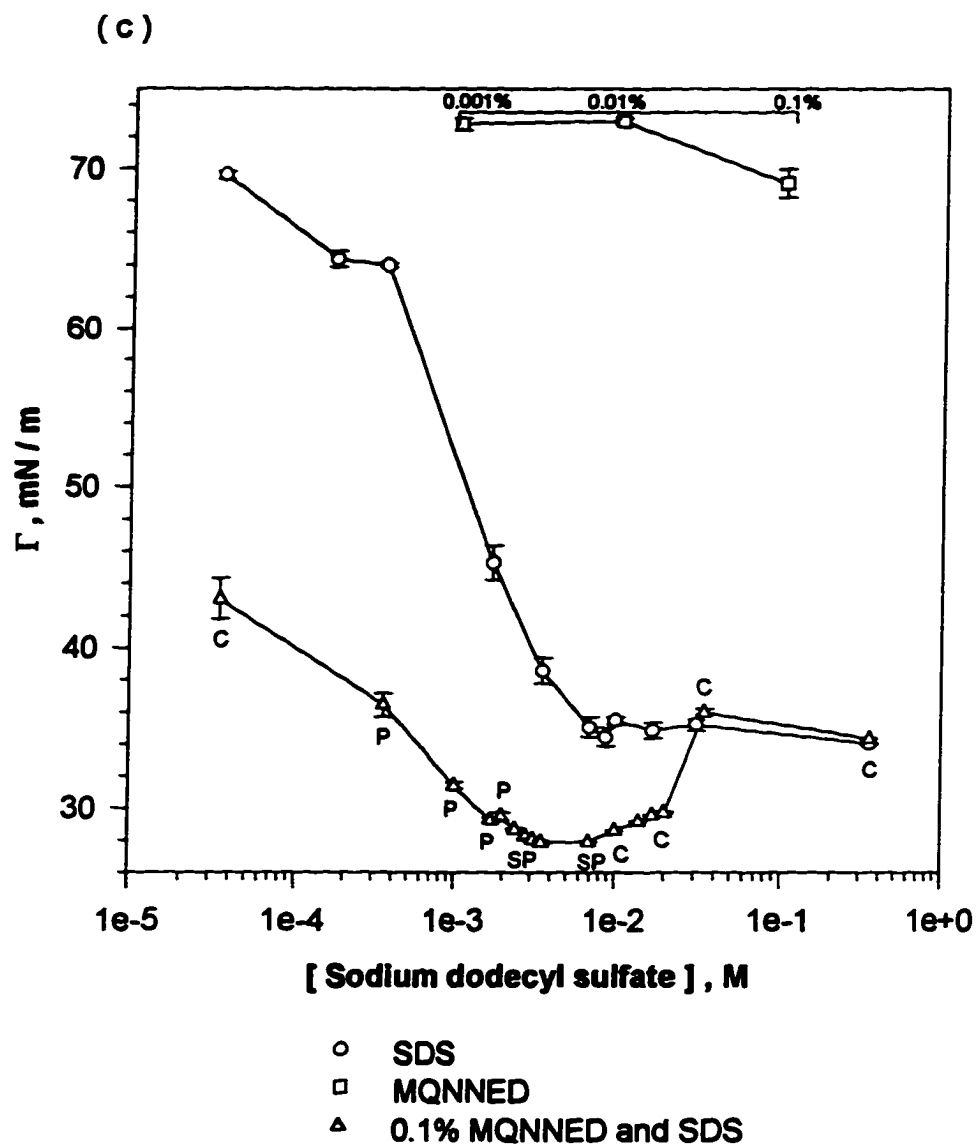
**Symbols indicate: C = clear solution, H = hazy solution,
SP = slight precipitate, and P = precipitate.**



(Figure continued)



(Figure continued)



Regardless of polymer architecture, the solutions that contained 0.1% polymer and SDS were more effective in reducing surface tension than SDS alone. This result indicates that the ability of the polymer - surfactant complex to reduce surface tension is dependent upon adsorption of the surfactant monomer at the cationic sites on the polymer.

The observed decreases in surface tension result from the formation of an insoluble surface active polymer - surfactant complex which partitions at the air/liquid interface (Figure 8.12). Addition of increasing amounts of surfactant results in further decreases in surface tension as the air/liquid interface becomes saturated until a monolayer of surfactant is adsorbed by the polymer. Upon adsorption of a monolayer of surfactant, the polymer - surfactant complex precipitates maximally and surface tension increases. Beyond this point of maximum precipitation, surface tension again begins to decrease as the concentration of free surfactant in solution controls the surface tension of the liquid. Surface tension of the polymer - surfactant solutions eventually coincides with the surface tension of the surfactant as the precipitated complex is resolubilized by formation of polymer bound micelles and free micelles.

8.9 CONCLUSIONS

When a slightly surface active polymer is added to a surfactant solution, reduction of surface tension occurs due to formation of a highly surface active complex. The evidence of this complexation is the formation of an insoluble precipitate which is more efficient at reducing surface tension than the surfactant alone. The surface tension plots show evidence of three interaction zones corresponding to formation of the surface

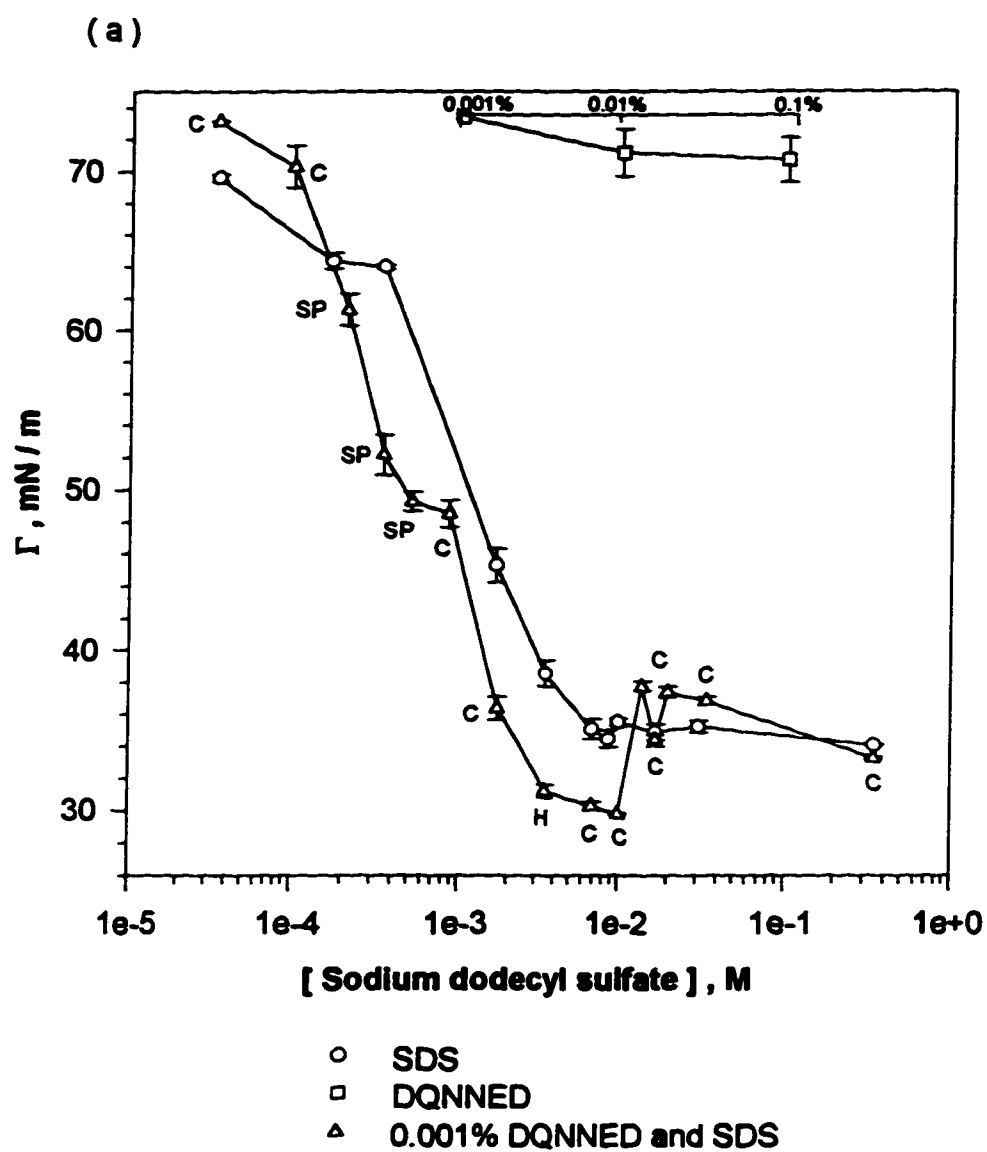
Figure 8.11: Surface Tension of DQNNED - SDS Complexes.

(a) 0.001% DQNNED and SDS

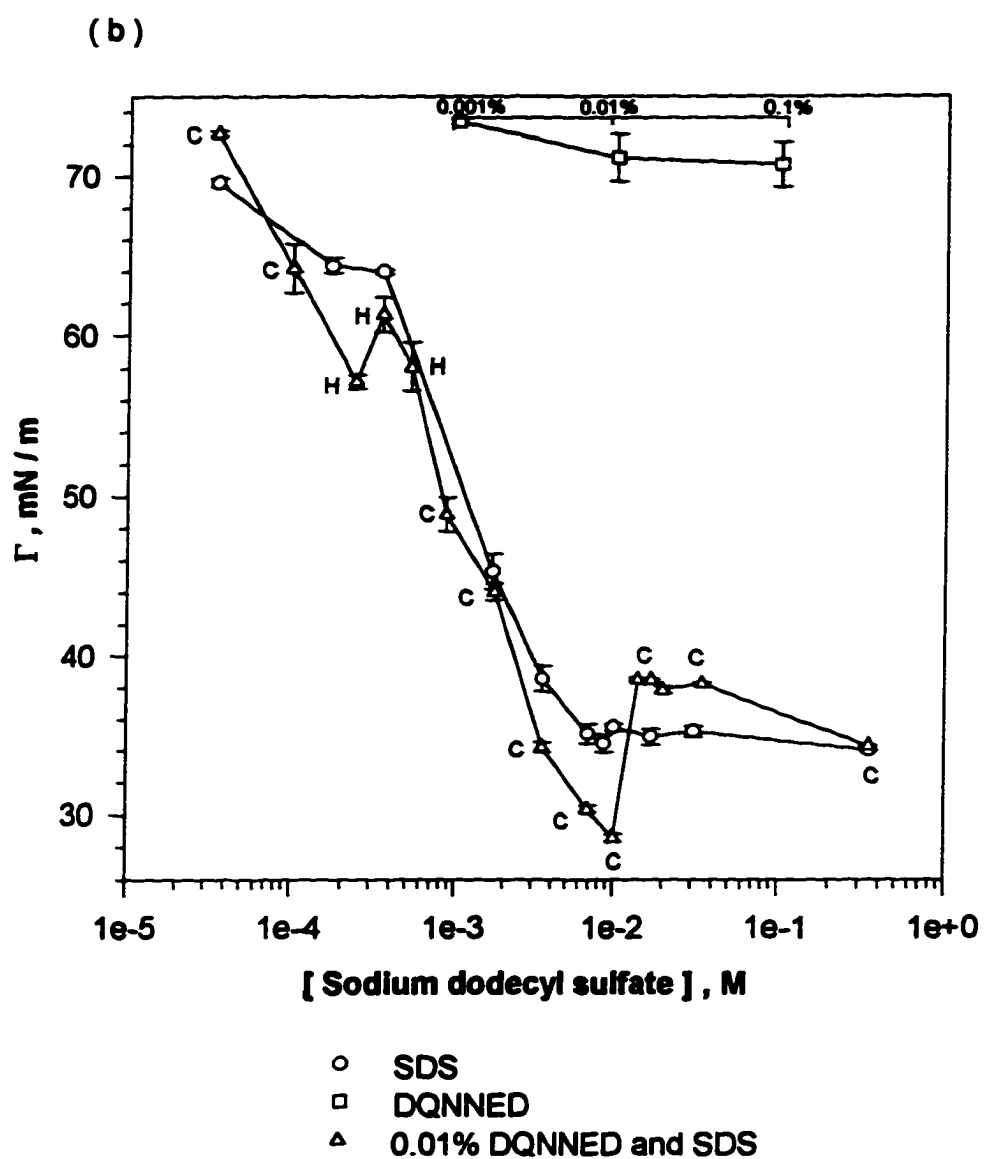
(b) 0.01% DQNNED and SDS

(c) 0.1% DQNNED and SDS

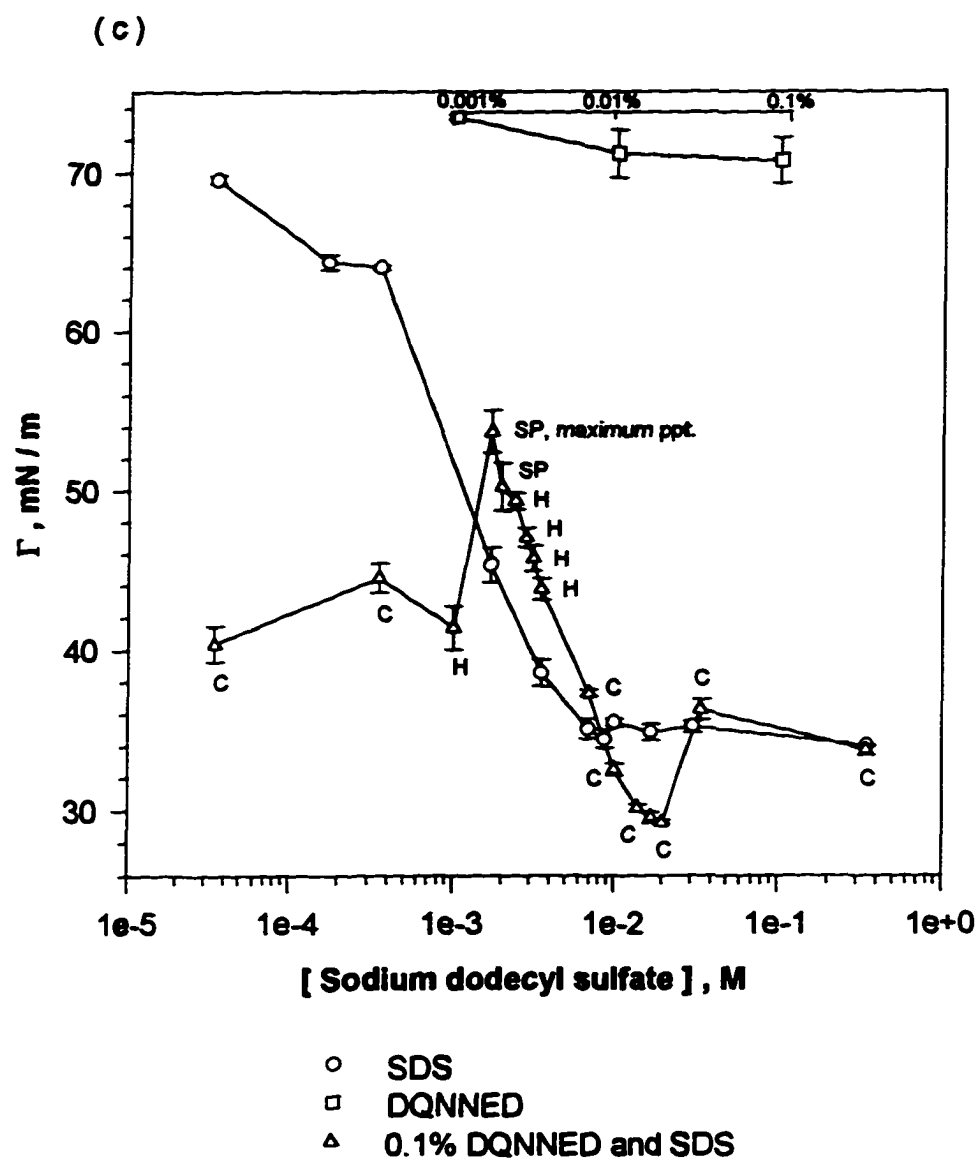
**Symbols indicate: C = clear solution, H = hazy solution,
SP = slight precipitate, and P = precipitate.**



(Figure continued)



(Figure continued)



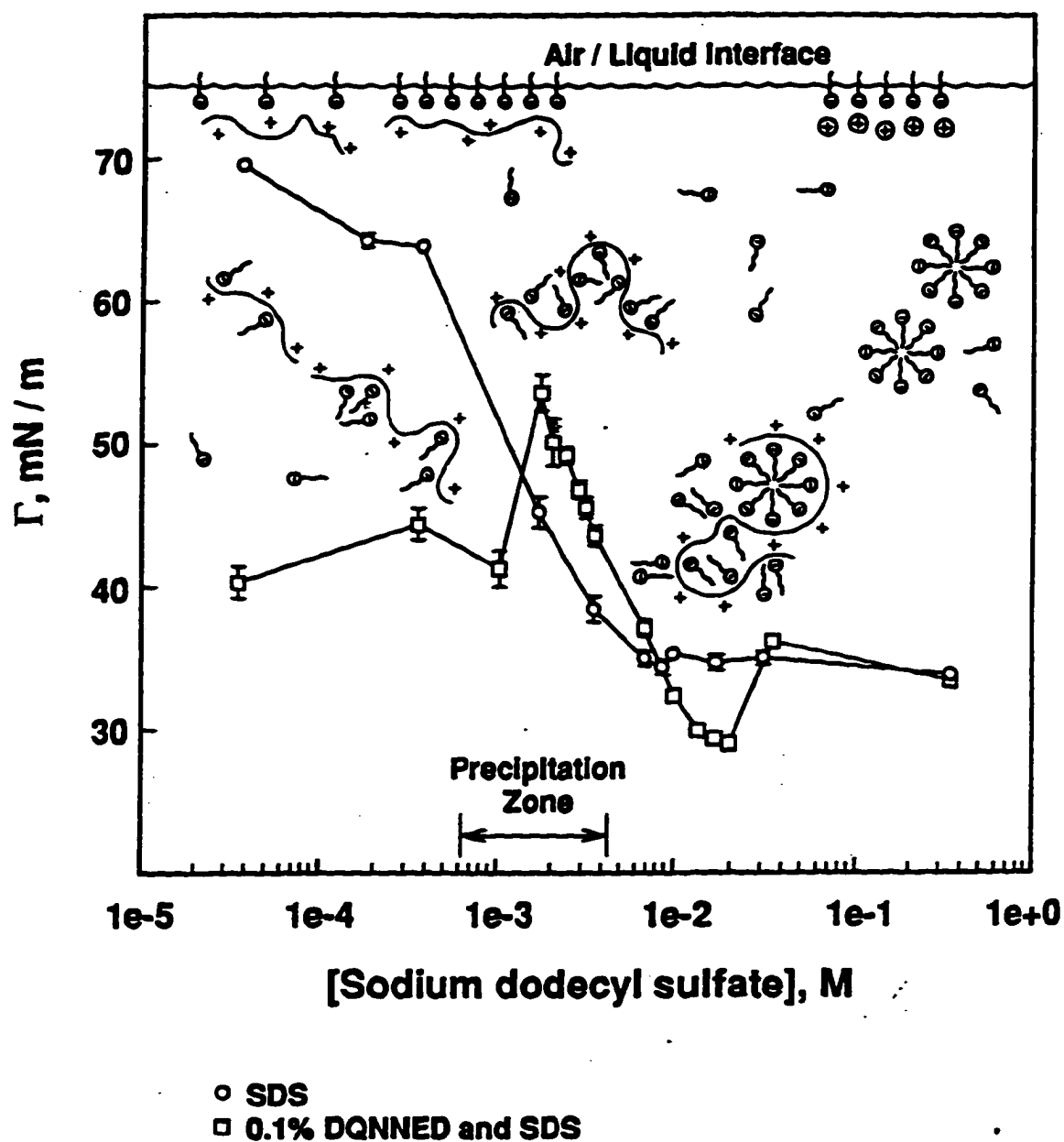


Figure 8.12: Conditions at the Air/Liquid Interface and in the Bulk Solution of a Solution Containing a Fixed Concentration of a Cationic Polymer and an Anionic Surfactant.

active complex, precipitation of the complex due to adsorption of a monolayer of surfactant monomer, and resolubilization of the complex. The interaction zones are present regardless of polymer structure or charge density. The ability of the polymer - surfactant complex to reduce surface tension appears to be independent of polymer architecture and dependent only upon adsorption of the surfactant species at the cationic polymer sites.

CHAPTER 9: FOAMS

9.1 INTRODUCTION

Foams have been known since the discovery was made that animal fats when mixed with ashes yield a product with the ability to cleanse clothing.¹⁵¹ Nature also makes use of foams for protection of immature insects such as the cuckoo-spit.¹⁵¹ Today, most people know what is a foam from simple every day experiences such as shaving, enjoying a cold beer, taking a bubble bath or watching the foam break as the waves hit the seashore. Industrially, foams have found use in fire extinguishers, gas-liquid extraction, fractionation, froth flocculation for the separation of minerals, retention of particulate matter in the air and in petroleum operations such as drilling of oil wells and enhanced oil recovery.¹⁵² The cosmetics industry in particular has made much use of foam technology in shaving creams, shampoos and detergents, bubble baths, mousses and toothpastes to name a few applications. It is the objective of this work to study the effects of water soluble quaternary compounds on foam stability as they are widely utilized in the cosmetics industry.

9.2 BUBBLES

Bubbles are spherical or hemispherical envelopes of liquid enclosing air.¹⁵³ In this work a bubble will be referred to as a spherical or near spherical thin layer (lamellae) of liquid enclosing a gas. The gas used may be air, nitrogen, carbon dioxide, propane or butane. The liquid layer can be water, a hydrocarbon or any other organic solvent.

9.3 FOAMS

Foams are simply aggregates of soap bubbles in a liquid matrix.^{151,154} They have also been described as relatively stable, coarse dispersions of gas in a small amount of

liquid.^{151,152,155} The gas-in-liquid dispersion must be stabilized by a surfactant.¹⁵² Foam is produced when air or another gas such as propane or butane is introduced beneath the surface of a surfactant solution. The adsorption of the surfactant monomers on the liquid/gas surface stabilizes the foam. Foam dissipates as the liquid drains away from the lamellae which surround the air globules until the film finally collapses.

Neither absolutely pure liquids^{94,151,152} nor mixtures of similar types of components produce foam.⁹⁴ Foams must contain a third component which is surface active (capable of being adsorbed at the liquid/gas, L/G, interface).^{94,151,152,155} The presence of a surfactant produces lamellae that have an adsorbed monolayer of surfactant molecules on each side of the L/G interface. These adsorbed films increase resistance to thinning of the lamellae. Film elasticity, resistance to thinning, is a necessary condition for the production of foam. However, elasticity alone is not sufficient for production of a persistent foam. Persistent foams exhibit lifetimes of hours to days while effervescent foams have lifetimes of a few seconds to a minute.⁹⁴

9.3.1 Thermodynamics of Foam

The requirement of a surfactant for foam production may be confirmed using a thermodynamic argument. Foams have surface area. This surface area is large enough to make a significant contribution to the total energy of the system. The Helmholtz function for foam includes the surface area, A , as an extensive variable (Eq. 9.1):

$$dF = -pdV - SdT + \gamma dA + \sum \mu_i dn_i \quad (9.1)$$

where γ is the surface tension of the liquid, μ_i and n_i are the chemical potential and concentrations of the various components, respectively.¹⁵²

Integration of Eq. 9.1 gives:

$$\Delta F = \gamma \Delta A + \int -p dV \quad (9.2)$$

where ΔF is the change of the Helmholtz free energy at constant T , n_1 and n_2 . Equation 9.2 indicates that a decrease of the free energy results from both expansion of the gas and reduction of surface area. This reinforces the concept that foam produced from a gas in a pure liquid is thermodynamically unstable.¹⁵²

There are three forms of surface active agent which may be used to produce foam. These are solutes, solid particles and liquid crystals. If the surfactant is a solute, it must be positively adsorbed at the L/G interface.¹⁵² Otherwise, if a finely divided solid is employed, the particles must remain at the surface due to a finite contact angle with the liquid.¹⁵² A liquid crystalline surfactant must exhibit a positive spreading coefficient in order to produce foam.^{152,156} Addition of a third component at the L/G interface requires that work be done on the system in order to transfer the component out of the surface. Addition of a work term, $W_{\text{desorption}}$, to the Helmholtz equation (9.2) yields:

$$\Delta F = \gamma \Delta A + \int -p dV + W_{\text{desorption}} \quad (9.3)$$

where the first 2 terms are related to drainage of the liquid and diffusion of gas out of bubbles. The work of desorption may cause the function to have a positive value; however, experimentally, nearly all foams are thermodynamically unstable.¹⁵²

Although thermodynamically unstable, foam may be kinetically stabilized using the hydrodynamic factor and film strength factor. The hydrodynamic factor influences the rate of drainage of liquid from the film-forming lamellae and the capillary section of the Plateau borders. Hydrodynamic flow within the lamellae can be controlled by

varying the fluid rheology and the foam geometry.¹⁵⁷ Interfacial viscoelastic properties in dilution affect the film strength factor as foam stability is affected by environmental disturbances.¹⁵⁸ The film strength factor gives self-healing ability to the lamellae which makes foam susceptible to environmental disturbances.

9.3.2 Structure

The structure of foam is quite complex. For a foam to exist there must be two contact phases present: the water below and the atmosphere above.¹⁵¹ Water provides a matrix for the foam and adheres the bubbles together. Foam has three general components. These are the bubbles, the surfactant film surrounding the bubbles and the thin aqueous structure also containing surfactant monomers (Figure 9.1).^{151,154}

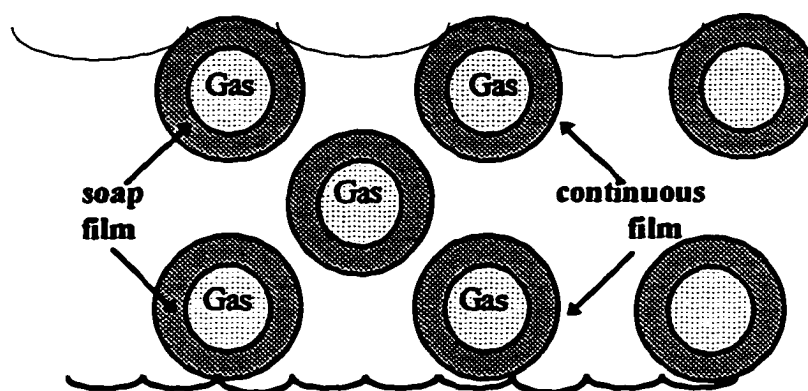


Figure 9.1: Structure of Foam.

9.3.3 Classification

Foams are classified as either effervescent (Kugelschaum) or polyhedric (Polyederschaum) dependent upon the volume of gas contained in the bubbles and the bubble shape. Effervescent foams contain a small amount of gas in the bubbles and the bubbles retain a spherical shape.^{151,159} Polyhedric foams contain a high volume ratio of

gas to liquid and the bubbles are deformed into a honeycomb structure.^{151,159} Polyhedric foam formation and stability is the focus of this work as they have many cosmetic applications.

Polyhedric foam has a honeycomb structure of gas cells whose walls consist of thin liquid films with approximately plane parallel sides (lamellae) (Figure 9.2).^{94,151} Where three or more bubbles meet in space the lamellae are curved. These concave areas of the lamellae are known as the Plateau borders or Gibbs triangles.

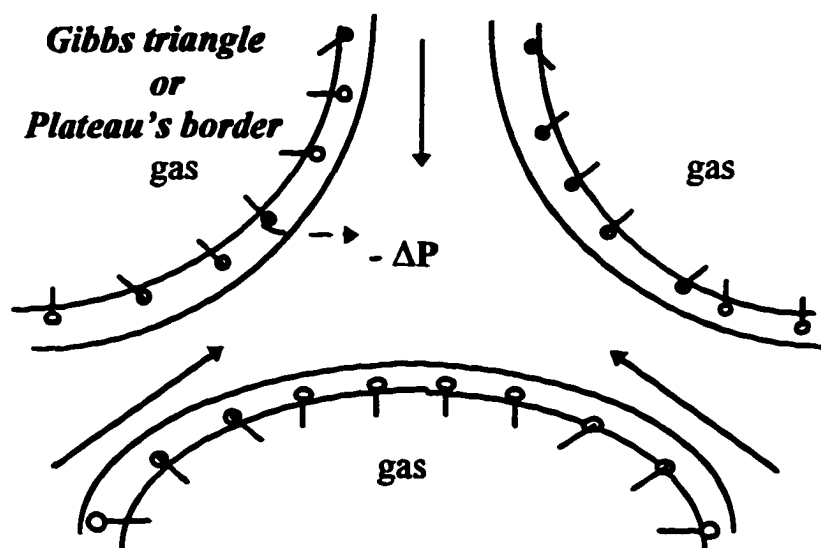


Figure 9.2: A Polyhedric Foam.

Plateau's laws are the two laws of bubble geometry that hold for all assemblies of bubbles and the morphology of foams. These laws are based on minimization of the surface area of liquid films.^{152,159,160} The laws are a direct result of the tension of the liquid surfaces. Plateau's laws are as follows: 1.) along an edge only three liquid lamellae meet, equally inclined, having dihedral angles equal 120° and 2.) at a point, four

of the edges meet equally inclined at a tetrahedral angle. If the foam structure is disturbed by film rupture, the bubbles will rearrange in order to conform to Plateau's laws.^{151,152}

The pressure difference across the Plateau borders resulting from the surface tension of the solution is given by the Laplace equation:

$$\Delta P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (9.4)$$

where r_1 and r_2 are the radii of the curved surface.^{94,152} The curvature of the lamellae is greatest in the Plateau borders. Therefore, the pressure across the interface is greater in these areas than anywhere else in the foam. Gas pressure inside an individual bubble is uniform whereas the liquid pressure inside the lamella at the Plateau border is lower than in the adjacent areas.⁹⁴ This pressure difference causes drainage of the liquid from the lamellae into the Plateau borders.¹⁵¹ In a column of foam, drainage also results from hydrostatic pressure. Therefore, the lamellae are thinnest in the upper region of the column and thickest in the lower region. Foams rupture as the liquid drains out of the lamellae which causes a progressive thinning of the lamellar surfaces. At a critical thickness of 50-100 Å the film collapses.^{94,152,155}

9.4 FOAM STABILITY

Foam stability is defined as the height of foam after a given amount of time.⁹⁴ Foamability and foam stability of surfactant solutions have been shown to be influenced by many factors such as the rate of liquid drainage,¹⁶⁰⁻¹⁶² the rate of gas diffusion,^{152,162} the rate of adsorption of surfactant to the L/G interface,¹⁵² size of bubbles,¹⁵² surface tension,^{152,160,163-165} viscosity^{156,160,161,163-165} electrolyte concentration,^{161,166,167} presence of

liquid crystals,¹⁵⁶ temperature,^{152,166,168} and pressure.^{152,167} Foam stability has been shown to increase as bulk viscosity of the foaming solution and surface viscosity of the adsorbed surfactant layer at the air/water interface are increased due to close packing of the molecules.¹⁶¹ Foam stability tends to decrease as the size distribution of bubbles, surface tension of solution, area/molecule of surfactant molecule, and diffusion coefficient of gas through the liquid film increases.^{154,159,162,166} Foam stability decreases in the presence of electrolyte, because the electrical repulsion between the ionic surfactant molecules at the interface decreases.^{155,167}

Nikolov and Wasan¹⁶⁷ observed stratification during thinning of liquid films formed from micellar solutions of anionic surfactant. This thinning was attributed to the layer-by-layer removal of an ordered structure of micellar layers from the film. The thickness of each thinning step was on the order of the diameter of the micelle together with the Debye atmosphere around it. The gradient of the chemical potential of micelles at the film periphery caused the stepwise thinning of the film.¹⁶⁹

Foamability, the volume of foam generated, has been reported to increase with temperature and decrease with the surface tension of the surfactant solutions.^{168,170} Oh and Shah¹⁵⁸ have shown that foamability of the micellar solution was influenced by the average lifetimes of the micelles. This occurs because micelles must be broken into monomer for adsorption onto the newly created surface of bubbles to occur.

Despite the fact that these factors have been studied separately, they are interdependent. There are four categories in which these factors may be primarily classified. These categories are the rate of drainage of the liquid, rate of gas diffusion, the thickness of the electrical double layer and surfactant chemical structure.

9.4.1 Rate of Drainage of Liquid

Drainage rate is defined as the rate at which the liquid drains from a foam whose lamellae are not broken during the process.¹⁵⁵ Drainage of the liquid contained in the lamellae causes thinning and leads to rupture of the foam. Gravity and surface tension cause the liquid to drain from the lamellae. However, the rate of drainage depends upon solution and surface viscosity,^{151,171} the surface tension of the solution⁹⁴ and repulsion of the lamellar films.¹⁵⁹ The rate of drainage may be reduced by the addition of viscosifying agents which increase the bulk and surface viscosities.^{156,161,172} Drainage by surface tension difference depends upon existence of pressure differences at various points in the lamellae due to the existence of Plateau borders.⁹⁴ The larger the difference between r_1 and r_2 (i.e. the larger the bubble size) and the higher the surface tension in the lamellae, the greater the pressure difference. Therefore, the rate of drainage is increased by higher pressure differences resulting from to different size bubbles in the foam. The rate of drainage can also be reduced if the two films repel each other when they come close together.¹⁵⁹ This can be accomplished by the addition of macromolecules which can sterically stabilize foam by increasing the viscosity^{159,162-165} and by bridging.¹⁶³⁻¹⁶⁵

9.4.2 Rate of Gas Diffusion

The rate of gas diffusion between bubbles is described by the following equation:

$$q = -JA \Delta P \quad (9.4)$$

where J is the permeability of the diffusion path, A is the effective perpendicular area through which diffusion occurs between bubbles and ΔP is the pressure difference of the two bubbles i.e. $\Delta P = 2 \gamma (1/r_1 - 1/r_2)$ and γ is the surface tension of the solution.⁹⁴ The negative sign indicates that gas diffusion is in the direction of pressure decrease

since the gas pressure is less in large bubbles.^{94,151,154,155} Therefore, large bubbles grow at the expense of small bubbles. The rate of gas diffusion is decreased by increasing the packing of surfactant molecules,⁹⁴ increasing the number of carbon atoms of the hydrophobic group,¹⁷³ or decreasing the molecular weight of hydrophilic group.¹⁷³

9.4.3 Thickness of the Electrical Double Layer

For anionic surfactants, electrostatic repulsion between two sides of the film and high osmotic pressure due to a large concentration of counterions present prevents thinning of foams.^{94,155,167} These factors have been suggested by the existence of persistent foams in cases where the film is not known to have great surface viscosity and is true of solutions of purified surfactants. When the film becomes thin, less than 200 nm, stability results from electrical repulsion between the double layers of the adsorbed ionic surfactant on the two sides of the film.⁹⁴ Addition of electrolyte causes compression of the electrical double layers and decreases the mutual repulsion which in turn decreases the stability.^{94,155,166,167}

9.4.4 Surfactant Chemical Structure

Foam stability is also determined by the nature and concentration of surfactant present in the solution.¹⁵¹ For a liquid to foam the membrane at the L/G interface must be elastic such that any applied stresses tending toward local thinning or stretching of the membrane are opposed and balanced by restoring forces.^{94,151} The restoring forces must increase with the amount of displacement. If the solution is too dilute, then the surface tension of the solution approaches that of the pure solvent.⁹⁴ Therefore, the restoring force will be too small to withstand thermal and mechanical shocks. If the surfactant concentration is too far above the CMC, the change in surface tension with increase in

area of the film will be too small to prevent rupture.⁹⁴ This is due to the fact that surface tension does not change above the CMC. Consequently, elasticity is compromised at extremes of surfactant concentration. Therefore, an optimum concentration for maximum foaming in any solution should exist. This maximum occurs at concentrations below the CMC of the surfactant.¹⁵¹

Gibbs elasticity is defined as the ratio of the increase in the film tension from an infinitesimal increase in area and the relative increment is given by

$$E = d\gamma / d \ln A = d\gamma / (dA/A) \quad (9.5)$$

where E = elasticity.¹⁵⁶ Therefore, the greater the elasticity the more stable is the bubble.¹⁵² Comparing one surfactant to another, those that form the least compressible monolayers are the most effective as bubble stabilizers.¹⁵²

Surfactant efficiency is described as the bulk phase concentration required to produce a significant amount of foam.⁹⁴ Foam height generally increases with surfactant concentration below the CMC until the CMC is reached where foam height is maximized within a given chemical type.⁹⁴ Surfactants with low CMC's are more efficient as foaming agents.^{94,155,167}

SDS has been extensively investigated with respect to its surface and micellar properties.¹⁵² Few known measurements of Gibbs surface elasticity have been made in aqueous SDS solutions.¹⁷⁴ A maximum in foam stability occurs at a concentration of half the CMC (4 mM). The foam stability of SDS decreases to zero and reaches a second and higher maximum at a concentration above the CMC after which a decrease in foam stability occurs.¹⁵²

Surfactant effectiveness is defined as the maximum foam height obtained with the surfactant solution regardless of its concentration.⁹⁴ Effectiveness is dependent upon ability to reduce the surface tension of solution. The lower the surface tension, the greater the volume of foam of the same size bubbles is produced.¹⁷⁵ For ionic surfactants, the effectiveness depends upon the type of counterion present. Smaller counterions have been shown to produce greater initial foam height and stability.⁹⁴

9.5 ADDITIVES THAT STABILIZE FOAM

Additives may be used to increase foam stability. These additives increase foam stability by decreasing the rate of surface tension equilibrium, increasing mechanical strength via close packing of surfactant molecules or adsorption in monolayers to produce a foam which has extremely thin lamellae prior to rupture.^{94,155,161,172}

Most effective for decreasing the rate of surface tension equilibrium are long chain water insoluble polar compounds with straight chain hydrocarbon groups of approximately the same length as surfactant (i.e. dodecanol).^{94,161,172} Studies on SDS have shown that addition of dodecanol increases foam stability by increasing the solution viscosity¹⁷⁶ and decreasing the rate of drainage.^{177,178}

Sawyer and Fowkes¹⁷⁹ have shown the order of susceptibility to stabilization as: primary alkyl sulfates > 2-n-alkanesulfonates > secondary alkyl sulfates > alkylbenzenesulfonates > branched alkylbenzenesulfonates. Effective foam stabilizers lower the CMC of surfactants. Salts of long chain amines are effective stabilizers due to the strong electrical attraction between cationic and anionic surfactant forming a closely packed surface film.¹⁸⁰

Water soluble polymers, such as proteins or long chain solutes, which adsorb at the surface in coherent monolayers produce foams that can drain to extremely thin lamellae before rupture.^{152,162} They also increase the viscosity of the solution and in turn foam stability by decreasing the rates of drainage and gas diffusion.¹⁶² Sarma et al.¹⁶² have shown that the addition of 0.75% sodium carboxymethyl cellulose (NaCMC) increases the drainage half life by greater than 10 fold. Further increases in the amount of NaCMC increased the drainage half-life. This is attributed to adsorbed layer possessing mechanical or flow properties that differ from the bulk solution.

The role of polyelectrolytes and oppositely charged surfactants with respect to foam stability have recently been studied.^{52,163-165} These studies indicate that the formation of surface active complexes has a profound effect on both stability and foamability of SDS solutions.

9.6 EXPERIMENTAL

10 ml of each solution was prepared and placed in a glass-stoppered 25 ml graduated cylinder. The cylinder was shaken ten times by hand through an arc of 180 degrees. The initial volume of foam produced was recorded and additional measurements were made at 30 minutes, 1, 6, and 24 hours following the method of Goddard and Hannan.⁵²

9.7 RESULTS AND DISCUSSION

9.7.1 Effect of Polyquaternium 10 on Foam Stability of Sodium Dodecyl Sulfate

The foaming of solutions of polymers and sodium dodecyl sulfate (SDS) alone was studied in order to determine a baseline for foam height. The results (Table 9.1) indicate that Polyquaternium 10 foams slightly as it is slightly surface active. Whereas

Table 9.1: Foam Height of Polymer or Sodium Dodecyl Sulfate Solutions

| Polymer % | SDS % | initial (mm) | 30 min. (mm) | 1 hour (mm) | 6 hours (mm) | 24 hours (mm) |
|------------------------------|------------------|---------------------------|-------------------------------|------------------------------|-------------------------------|--------------------------------|
| 0 | 10 | 117.5 ± 10 | 92.5 ± 8 | 87 ± 7 | 69 ± 0 | 0 ± 0 |
| 0 | 1 | 84 ± 6 | 72.5 ± 3 | 57.5 ± 3 | 44.5 ± 3 | 16 ± 1 |
| 0 | 0.1 | 93 ± 5 | 66 ± 4 | 47.5 ± 3 | 34.5 ± 5 | 9 ± 1 |
| 0 | 0.01 | 4 ± 1 | 2 ± 1 | 0.5 ± 1 | 0 ± 0 | 0 ± 0 |
| 0 | 0.001 | 1.5 ± 1 | 1 ± 1 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| Polyquaternium 10 | | | | | | |
| 1 | 0 | 6 ± 0 | 4 ± 0 | 3.5 ± 1 | 3 ± 1 | 0 ± 0 |
| 0.1 | 0 | 9.5 ± 5 | 2.5 ± 2 | 1.5 ± 2 | 0.5 ± 1 | 0 ± 0 |
| 0.01 | 0 | 3 ± 1 | 1 ± 1 | 1 ± 1 | 0 ± 0 | 0 ± 0 |
| 0.001 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| MQNED | | | | | | |
| 1 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| 0.1 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| 0.01 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| 0.001 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| DQNNED | | | | | | |
| 1 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| 0.1 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| 0.01 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |
| 0.001 | 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 | 0 ± 0 |

neither MQNNED nor DQNNED produced any foams, neither stable nor even metastable. Therefore, increases in foaming and foam stability for systems of cationic polymer and SDS can be attributed to the formation of the polymer - surfactant complex, or stabilization or enhancement of the adsorbed surfactant layer by the presence of the polymer. This result agrees with the findings of Ross and Nishioka ¹⁸¹ who state that solvents that readily dissolve polymer (i.e. good solvents) do not make foamy solutions whereas solvents that dissolve polymer less readily (i.e. theta solvents) make foamy solutions. Declining interaction between solvent and polymer is said to lead first to enhanced surface activity as evidenced by increasing foam stability, followed by a severe reduction of solubility of the polymer that the foam stability is reduced due to the lack of concentration of the active component.

As the concentration of SDS was increased, the maximum initial foam height (foamability) also increased up to 0.1% SDS (3.5 mM). Foam height then decreased slightly at 1% SDS given the standard deviations from the measured foam heights observed. As the concentration was increased further to 10% (350 mM), the maximum initial foam height was observed. Foamability increases as surface tension decreases; therefore, solutions above the CMC should produce the greatest amounts of foam as surface tension is minimized. These results agree with results reported by Oh and Shah ¹⁵⁸ on the relationship between micellar lifetime and foamability. Their results indicate that micellar lifetime reaches a maximum at 200 mM SDS while foamability is minimized due to the stability of the micelles. At 800 mM SDS, micellar lifetime was minimized and foam height reached a maximum value. Therefore the most effective concentration of our solutions studied is 10% SDS which produced the maximum initial foam height.

After 24 hours, foam stability, the maximum foam height obtained at a particular time, was produced by the 1% SDS solution. This result disagrees with previously reported results which indicate that a maximum in foam stability occurs at half the CMC for SDS (4 mM).¹⁵² Foam stability is then reported to decrease to zero and reach a higher maximum stability at concentrations greater than the CMC. These previous results for SDS were predicted using foaming of butyric acid as a model system¹⁵² and may be the cause of the discrepancy with our data.

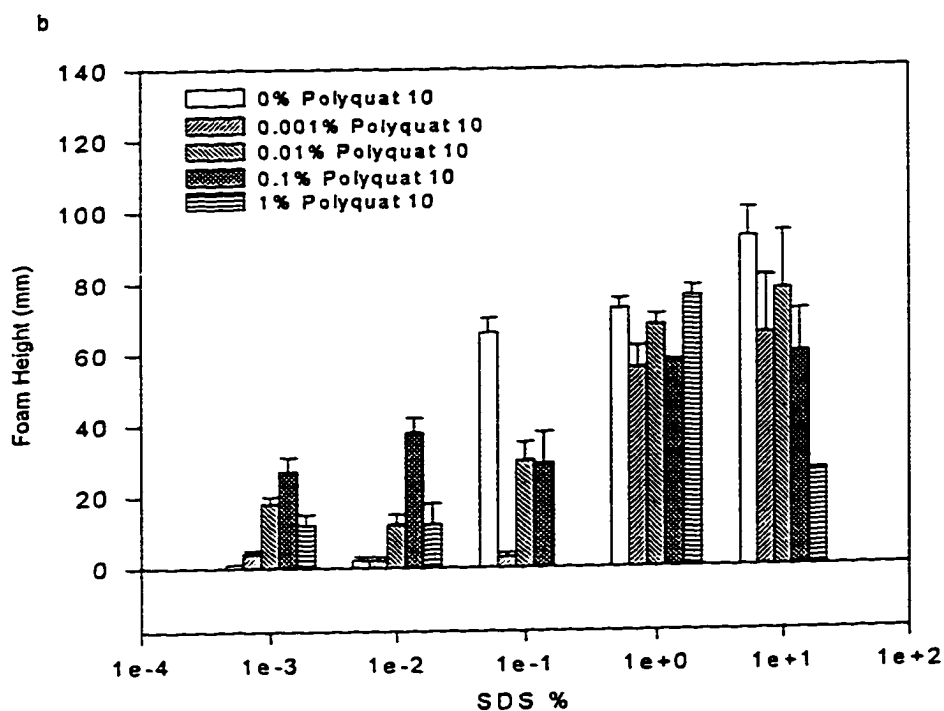
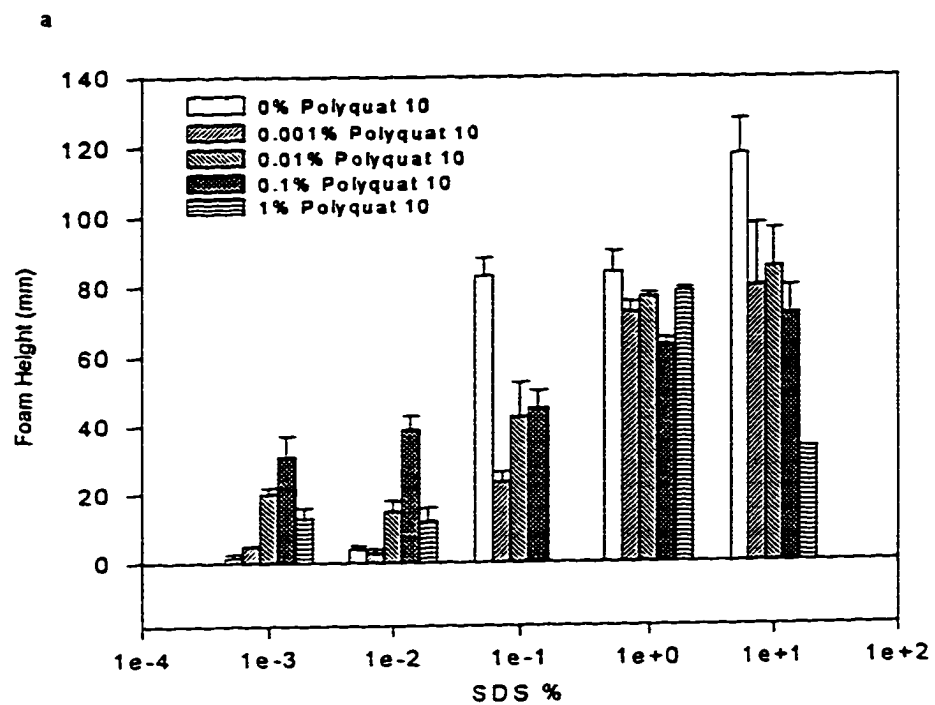
Foaming of SDS solutions is expected to be influenced by the addition of a water-soluble polymer⁵² as changes in viscosity and surface tension accompany changes in foam stability.^{156,160,161,163-165} Goddard and Hannan⁵² have shown that addition of Polyquaternium 10 to SDS solutions (0.001 - 0.1%) had a profound effect on foam stability after 30 minutes. The addition of 0.1% Polyquaternium 10 produced maximal increases in both foam height and foam stability.

For our studies, the concentration of Polyquaternium 10 and SDS was varied from 0.001 - 1% and 0.001 - 10%, respectively. Foam height and foam stability of the solutions were determined over the course of 24 hours. Initially, the overall maxima in foam height appears to be observed for the systems containing 0.001 - 1% Polyquaternium 10 and 1% SDS (Figure 9.3a). However, if the data are normalized to the amount of foam produced by SDS solutions alone (Figure 9.4), then maximal foaming occurs at low concentrations of SDS (0.001 - 0.1%).

$$\text{Normalized foam height} = \frac{\text{Foam height of solution with polymer (mm)}}{\text{Foam height of equivalent SDS solution (mm)}}$$

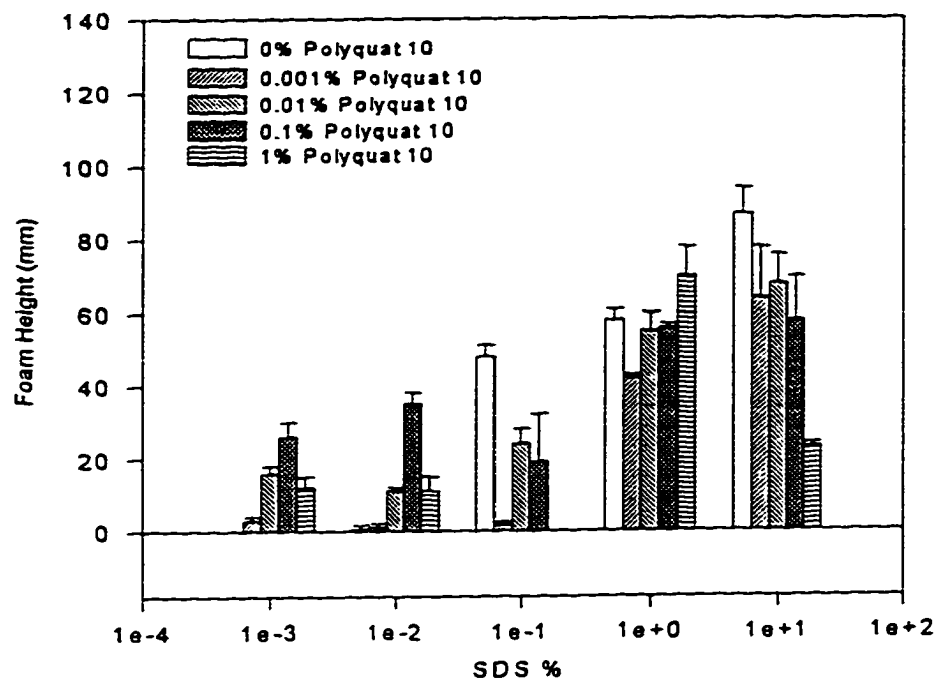
Figure 9.3: Determination of Foam Height for Polyquaternium 10 and SDS

- (a) initial**
- (b) 30 minutes elapsed**
- (c) 1 hour elapsed**
- (d) 6 hours elapsed**
- (e) 24 hours elapsed**

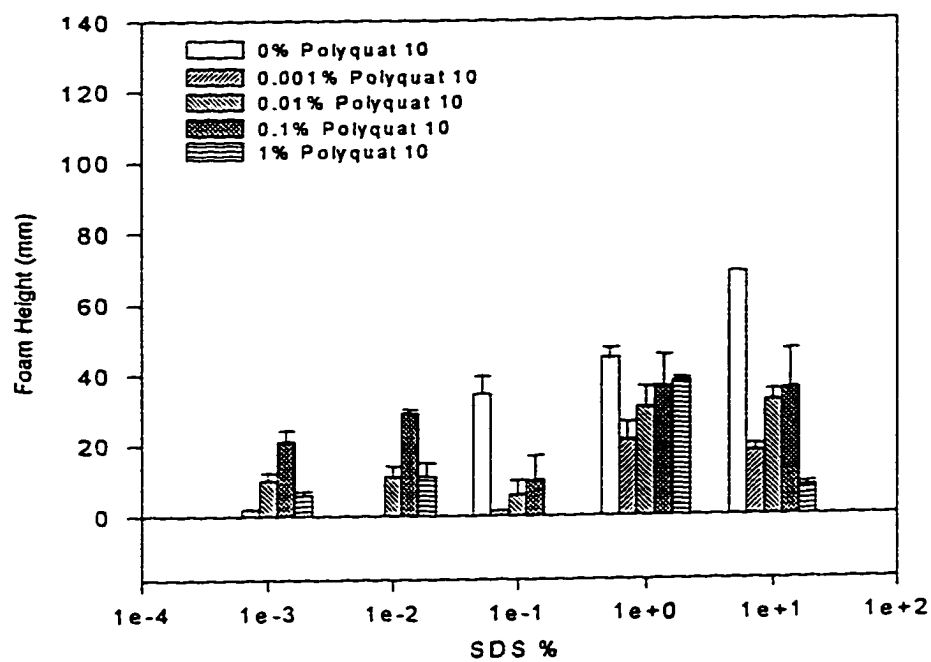


(Figure continued)

c



d



(Figure continued)

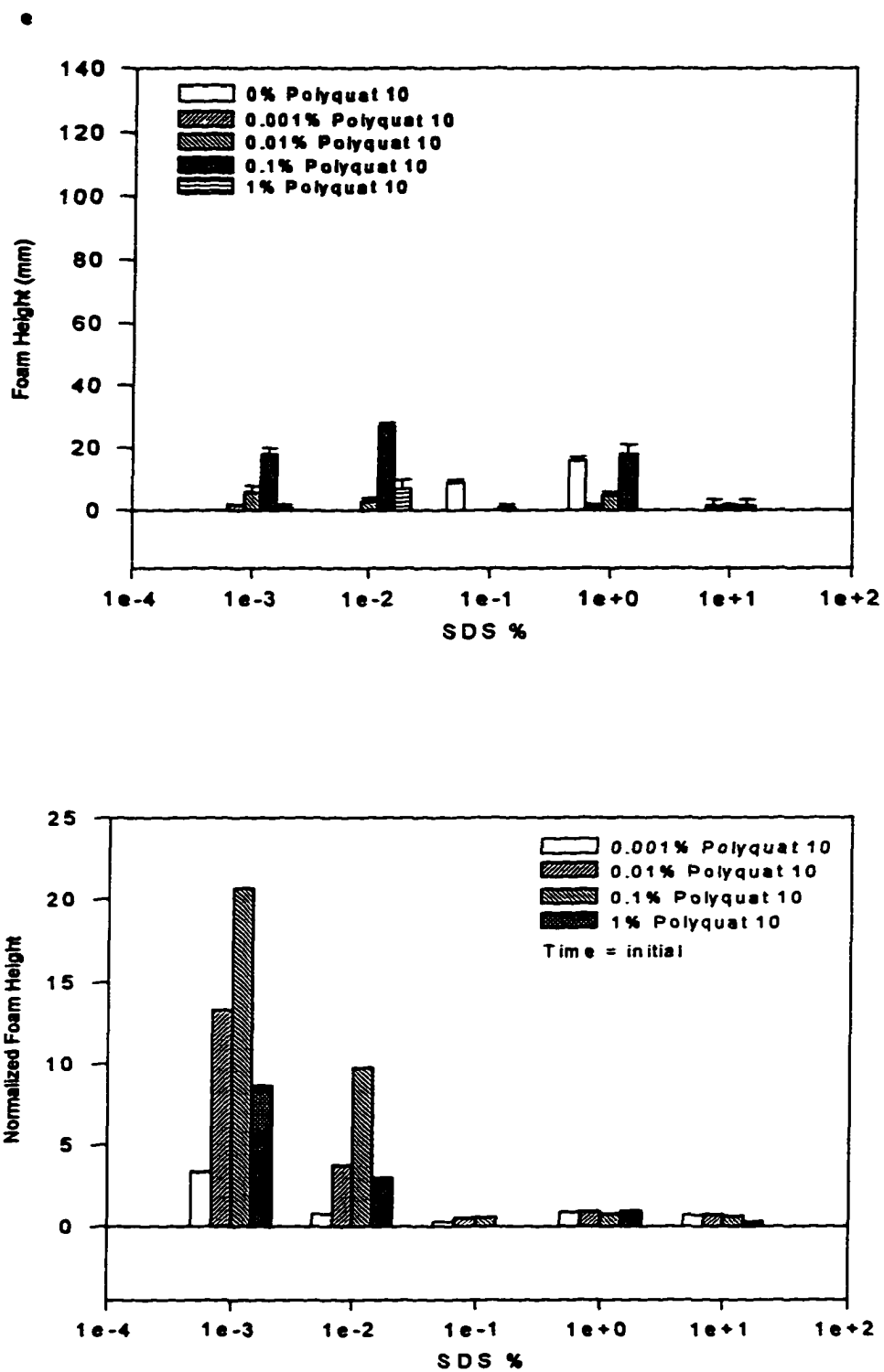


Figure 9.4: Foam Height Normalized for Amount of Foam Produced by SDS Alone.

Table 9.2: Half-lives, Surface Tension and Specific Viscosity for Systems of Polyquaternium 10 and SDS

| Polyquaternium 10 % | SDS % | slope = k sec ⁻¹ | time sec | hours | γ @ 22°C mN / m | η specific |
|---------------------------|----------|--------------------------------|-------------|--------|---------------------------|-----------------|
| 0.001 | 0.001 | -3.47 e-6 | 1.99 e5 | 55.49 | 64.80 | -0.001 |
| 0.01 | 0.001 | -7.70 e-6 | 9.00 e4 | 25.01 | 59.93 | 0.003 |
| 0.1 | 0.001 | -2.26 e-6 | 3.06 e5 | 85.20 | 45.21 | 1.380 |
| 1 | 0.001 | -1.00 e-5 | 6.93 e4 | 19.25 | 54.35 | 22.150 |
| 0.001 | 0.01 | -1.30 e-5 | 5.33 e3 | 1.48 | 58.80 | -0.001 |
| 0.01 | 0.01 | -7.35 e-6 | 9.43 e4 | 26.20 | 51.50 | 0.002 |
| 0.1 | 0.01 | -1.66 e-6 | 4.18 e5 | 116.23 | 46.36 | 1.840 |
| 1 | 0.01 | -2.60 e-6 | 2.65 e5 | 73.62 | 41.00 | 77.800 |
| 0.001 | 0.1 | -3.30 e-5 | 2.10 e3 | 0.58 | 31.40 | -0.001 |
| 0.01 | 0.1 | -4.00 e-5 | 1.73 e4 | 4.81 | 33.16 | -0.140 |
| 0.1 | 0.1 | -2.00 e-5 | 3.46 e4 | 9.63 | 38.38 | N / A * |
| 1 | 0.1 | N / A | N / A | N / A | N / A | N / A ** |
| 0.001 | 1 | -2.00 e-5 | 3.46 e4 | 9.63 | 37.66 | 0.580 |
| 0.01 | 1 | -1.00 e-5 | 6.93 e4 | 19.25 | 38.37 | 0.580 |
| 0.1 | 1 | -6.05 e-6 | 1.14 e5 | 31.82 | 36.39 | 0.250 |
| 1 | 1 | -2.00 e-5 | 3.46 e4 | 9.63 | 39.40 | 43.850 |
| 0.001 | 10 | -2.00 e-5 | 3.46 e4 | 9.63 | 33.71 | 0.924 |
| 0.01 | 10 | -2.00 e-5 | 3.46 e4 | 9.63 | 34.53 | 0.970 |
| 0.1 | 10 | -2.00 e-5 | 3.46 e4 | 9.63 | 32.49 | 1.790 |
| 1 | 10 | -3.00 e-5 | 2.31 e4 | 6.42 | 32.46 | 33.430 |

N/A = not applicable

N/A * this solution contained precipitated material and could not be determined by Ubbelohde

N/A ** this solution was a gel; therefore no determinations could be made

Addition of 0.1% Polyquaternium 10 produces the greatest increase in foam.

This result agrees with the results reported by Goddard and Hannan for the same system.⁵² Foaming of higher concentrations of SDS is destabilized by the addition of Polyquaternium 10. Over time, the foam height for all solutions studied decreases

(Figure 9.3a - e). After 24 hours elapsed, the solution containing 0.01% SDS and 0.1% Polyquaternium 10 contained the maximal amount of foam.

From the data the half-life, $t_{1/2}$, may be determined from semi-logarithm plots of foam height *versus* time. The slope of these plots yields the rate constant, k , for foam stability. The half-lives were determined from the data (Table 9.2). Analysis of this data indicates that foam stability is greatest for the solution containing 0.1% Polyquaternium 10 and 0.01% SDS as the half-life is approximately 116 hours (4 days, 20 hours, 14 minutes). The solution that decayed most rapidly contained 0.1% Polyquaternium 10 and 0.001% SDS having a half-life of 0.58 hours.

For solutions containing 0.001 - 0.01% SDS and 0.001 - 0.1% Polyquaternium 10, the foam stability as judged by $t_{1/2}$ increased as surface tension, γ , decreased and specific viscosity, η_{specific} , increased. This result agrees with previous results showing that increasing bulk viscosity¹⁶¹ and decreasing surface tension^{154,159,162,166} produce more stable foams. Increasing the viscosity by addition of polymer decreases the rate of liquid drainage in the lamellae thereby increasing foam stability.^{156,161,172} The lowering of surface tension as stability is increased is a result of bridging by polymer molecules which stabilize the foam.

All solutions containing 1% Polyquaternium 10 show a reduction in foam stability compared to the solutions containing similar amounts of surfactant. This is a result of the increased electrolyte concentration from the counterions associated with the polymer. The increase in counterion concentration decreases foam stability by compressing the electrical double layer.^{94,155,166,167}

These results differ from the work of Goddard and Hannan ⁵² who showed that maximum foaming was produced by solutions containing the maximal amount of precipitated material. We show that maximal foaming and foam stability occurs in those solutions nearest the plait point for the system Polyquaternium 10 / SDS / water. The plait point is the composition in a three or greater component system at which the two phases form one phase. For our system, as represented by a two dimensional phase diagram (Figure 9.5), the plait point would be a composition bordering the transition

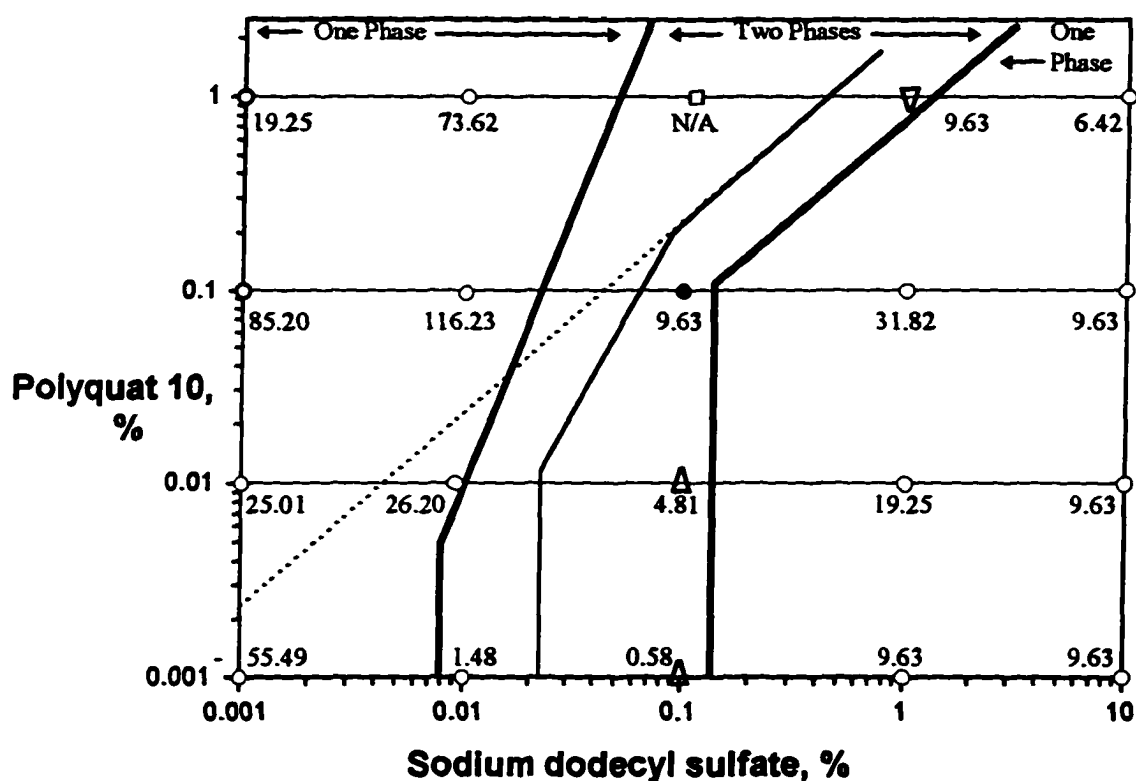


Figure 9.5: Phase Diagram and Foam Half-life for SDS / Water / Polyquaternium 10. Symbols indicate: ○ clear solution; ● precipitate; ▽ slight precipitate; △ hazy solution; □ gel; - - - - Theoretical charge neutralization; and ——— Maximum precipitate observed.

between clear one phase and hazy or precipitated two phase systems. This result agrees with the findings of Ross and Nishioka ¹⁸¹⁻¹⁸⁴ who state that surface activity is the precursor of phase separation and results in increasing foaminess of unsaturated solutions as they approach the solubility curve, with maximal foaminess occurring near the plait point. The precipitated phase is purported to destroy the foam of the parent phase if it is present as the dispersed phase or has a surface tension lower than the continuous phase. This thesis is obeyed for systems of Polyquaternium 10 / SDS as the half-life value decreases as the concentration of SDS increases. As the concentration of SDS is increased towards a critical point, the polymer is titrated out of solution by neutralization of the positive charges. Therefore, the polymer-surfactant complex can no longer increase foam stability by its presence at the foam/liquid interface.

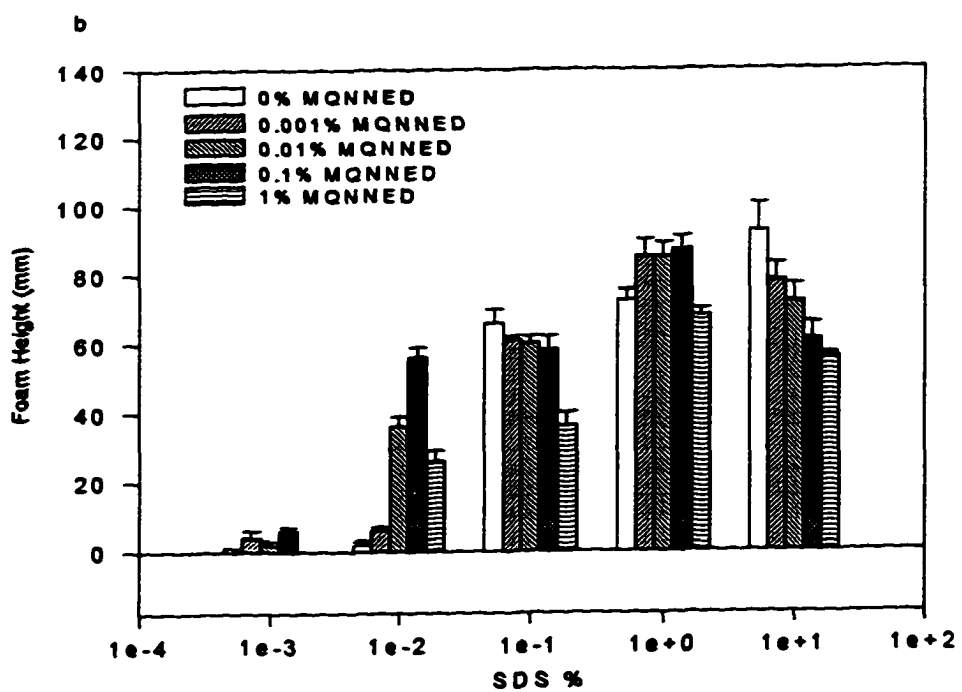
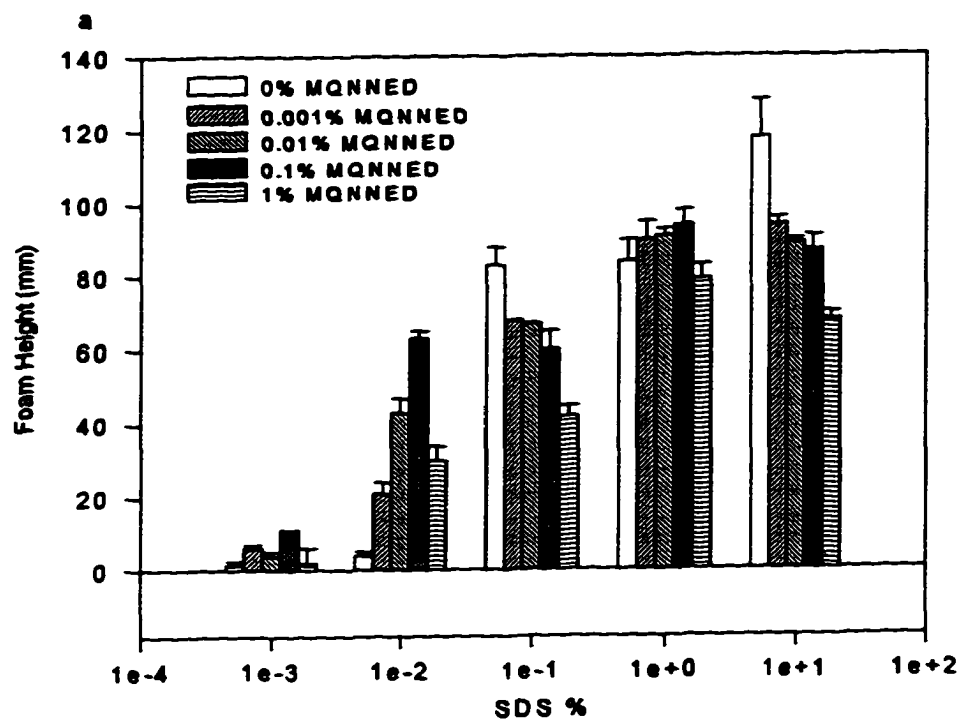
9.7.2 Effect to MQNNED on Foam Stability of Sodium Dodecyl Sulfate

Similar to Polyquaternium 10, the concentrations for MQNNED and SDS were varied from 0.001 - 1% and 0.001 - 10%, respectively. Initially, the overall maxima in foam height appears to be observed for the systems containing 0.001 - 1% MQNNED and 1% SDS (Figure 9.6a). However, when the data are normalized to the amount of foam produced by SDS solutions alone (Figure 9.7), the maximal foaming occurs at 0.1% MQNNED and 0.01% SDS. The addition of 0.1% polymer again produced the greatest increase in foam. Foaming of SDS was again destabilized by the addition of MQNNED.

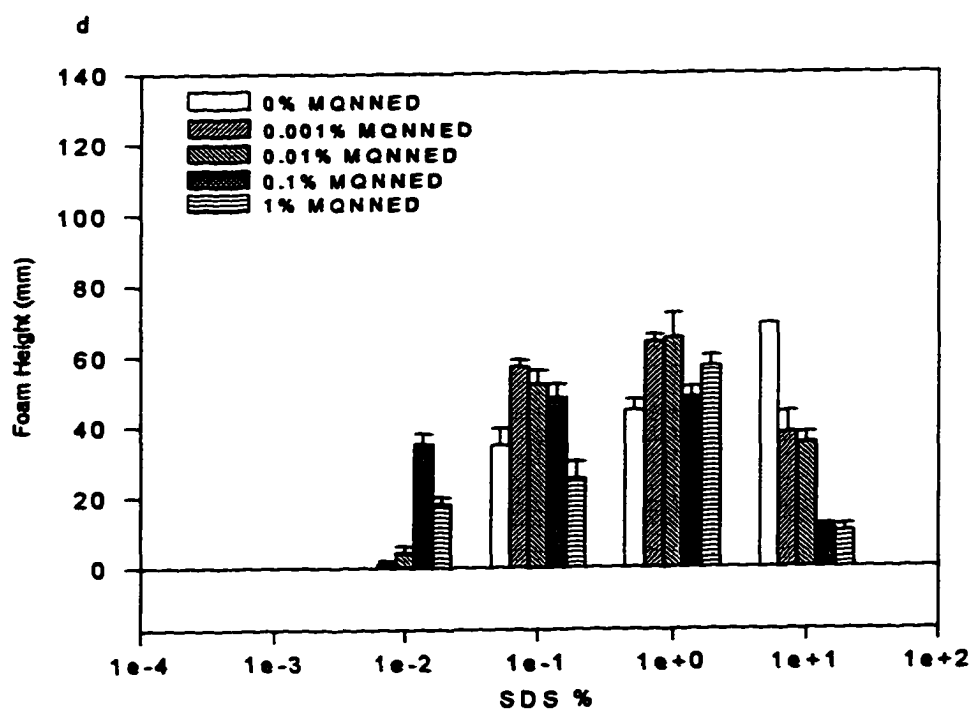
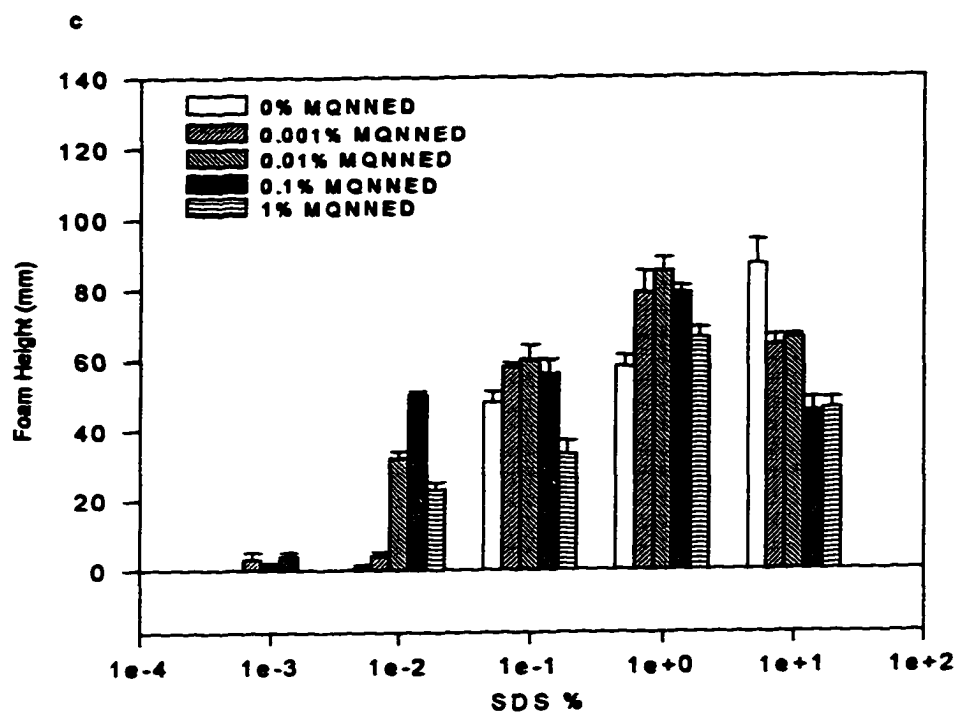
Over time, the foam height of all solutions was decreased (Figure 9.6a-e). After 24 hours, the solution containing 0.01% MQNNED and 0.1% SDS contained the maximal amount of foam. This is a 10 fold decrease in the amount of polymer required

Figure 9.6: Determination of Foam Height for MQNNED and SDS

- (a) initial
- (b) 30 minutes elapsed
- (c) 1 hour elapsed
- (d) 6 hours elapsed
- (e) 24 hours elapsed



(Figure continued)



(Figure continued)

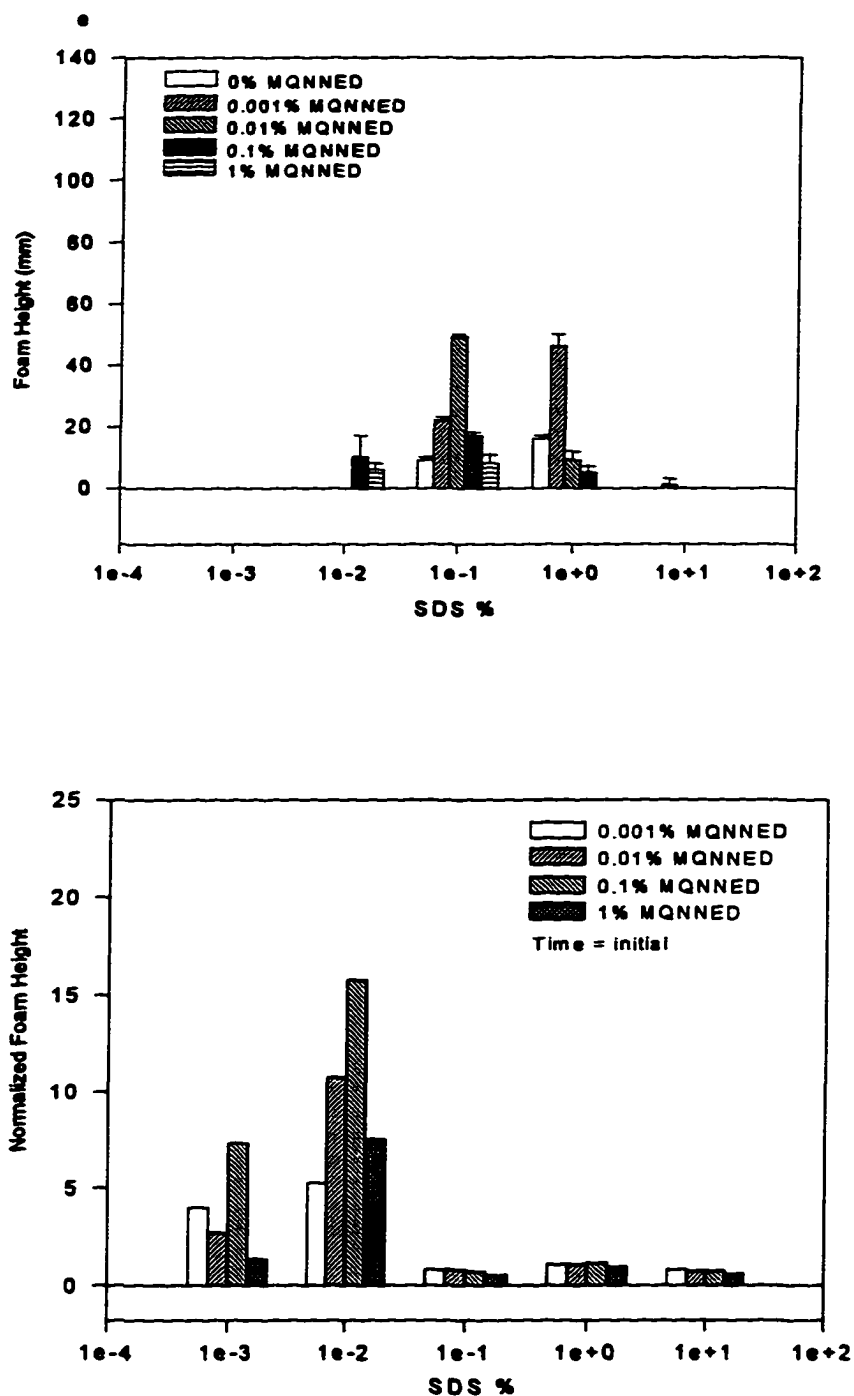


Figure 9.7: Foam Height Normalized for Amount of Foam Produced by SDS Alone.

Table 9.3 Half-lives, Surface Tension and Specific Viscosity for Systems of MQNNED and SDS

| MQNNED % | SDS % | slope = k sec⁻¹ | time sec | hours | γ @ 22°C mN / m | η specific |
|---------------------------|------------------------|---|---------------------------|--------------|----------------------------------|-------------------|
| 0.001 | 0.001 | -8.00 e-5 | 8.66 e3 | 2.41 | 72.82 | -0.001 |
| 0.01 | 0.001 | -1.70 e-4 | 4.07 e3 | 1.13 | 61.24 | 0.033 |
| 0.1 | 0.001 | -1.20 e-4 | 5.77 e3 | 1.60 | 43.04 | 0.210 |
| 1 | 0.001 | N / A | <1.80 e3 | < 0.5 | 50.73 | 1.760 |
| 0.001 | 0.01 | -5.00 e-5 | 1.38 e4 | 3.85 | 53.58 | -0.001 |
| 0.01 | 0.01 | -5.00 e-5 | 1.38 e4 | 3.85 | 45.54 | 0.046 |
| 0.1 | 0.01 | -8.87 e-6 | 7.81 e4 | 21.71 | 36.46 | 0.200 |
| 1 | 0.01 | -7.59 e-6 | 9.13 e4 | 25.37 | 32.77 | 1.870 |
| 0.001 | 0.1 | -5.36 e-6 | 1.29 e5 | 35.92 | 31.34 | -0.022 |
| 0.01 | 0.1 | -1.23 e-6 | 5.63 e5 | 156.54 | 31.13 | 0.020 |
| 0.1 | 0.1 | -6.31 e-6 | 1.09 e5 | 30.51 | 27.86 | 0.280 |
| 1 | 0.1 | -7.86 e-6 | 8.81 e4 | 24.50 | 29.88 | N / A * |
| 0.001 | 1 | -3.13 e-6 | 2.21 e5 | 61.51 | 38.36 | 0.024 |
| 0.01 | 1 | -1.00 e-5 | 6.93 e4 | 19.25 | 37.21 | 0.075 |
| 0.1 | 1 | -1.00 e-5 | 6.93 e4 | 19.25 | 36.01 | 0.240 |
| 1 | 1 | -5.11 e-6 | 1.35 e5 | 37.68 | 30.68 | N / A * |
| 0.001 | 10 | -2.00 e-5 | 3.46 e4 | 9.63 | 34.80 | 0.850 |
| 0.01 | 10 | -2.00 e-5 | 3.46 e4 | 9.63 | 34.36 | 0.088 |
| 0.1 | 10 | -4.00 e-5 | 1.73 e4 | 4.81 | 34.33 | 1.080 |
| 1 | 10 | -4.00 e-5 | 1.73 e4 | 4.81 | 31.87 | 4.240 |

N/A = not applicable

N/A * this solution contained precipitated material and could not be determined by Ubbelohde

to stabilize 0.1% SDS. Therefore, a lower concentration of polymer is required to stabilize the same concentration of SDS when the polymer contains a positive charge closely associated with the polymer backbone per cellulose unit.

Analysis of the half-life data (Table 9.3) indicates that foam stability is greatest for the solution containing 0.01% MQNNED and 0.1% SDS. The half-life is 156.54 hours (6 days, 12 hours, 32 minutes). The solution that decayed most rapidly contained 1% MQNNED and 0.001% SDS having a half-life less than 0.50 hours. For all the solutions studied, the specific viscosity increased and surface tension decreased as the concentration of MQNNED was increased. The systems nearest the plait point (Figure 9.8), those containing 0.01 or 0.1% SDS, exhibited an increase in foam stability. This

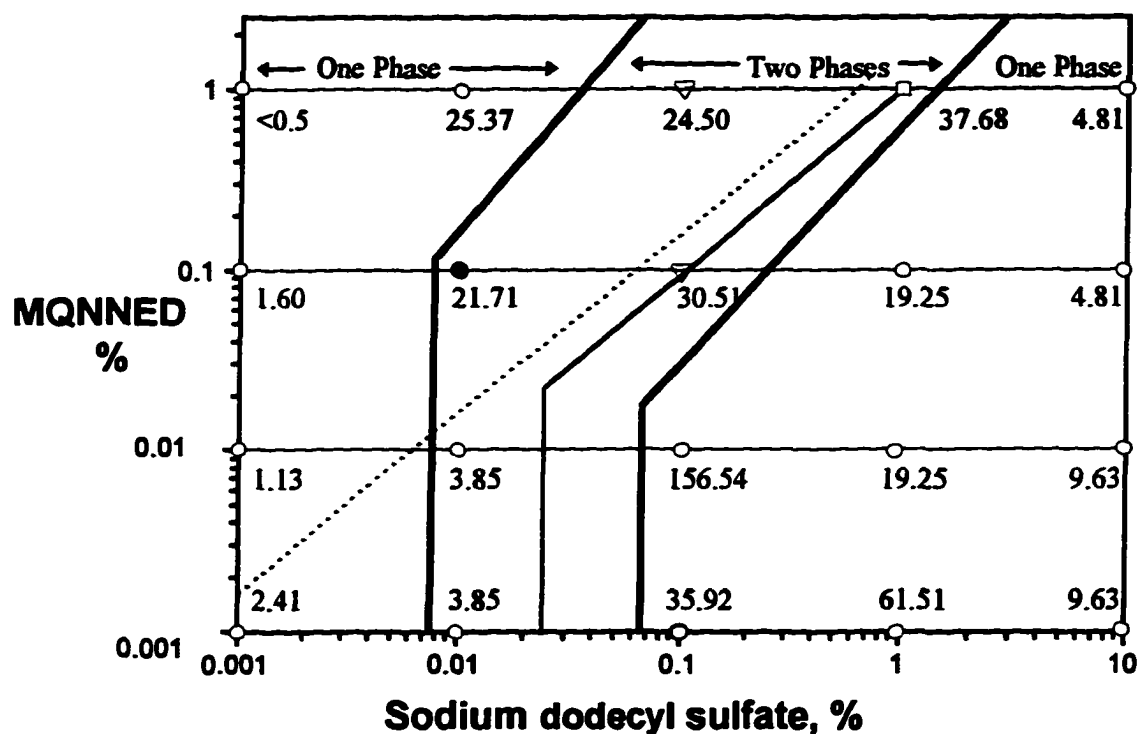


Figure 9.8: Phase Diagram and Foam Half-life for SDS / Water / MQNNED.

Symbols indicate: ○ clear solution; ● precipitate; ▽ slight precipitate; △ hazy solution; □ gel; - - - - - Theoretical charge neutralization; and - - - - - Maximum precipitate observed.

result agrees with the work of Ross and Nishioka¹⁸¹⁻¹⁸⁴ and indicates that maximal foaminess is reached near the plait point composition regardless of rigidity of the cellulose graft.

9.7.3 Effect of DQNNED on Foam Stability of Sodium Dodecyl Sulfate

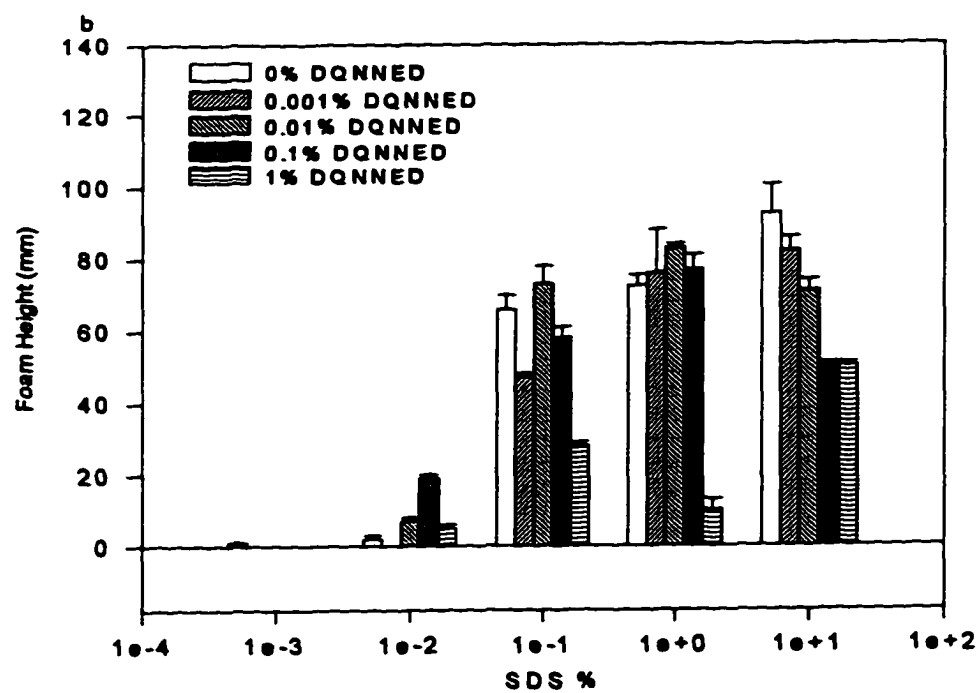
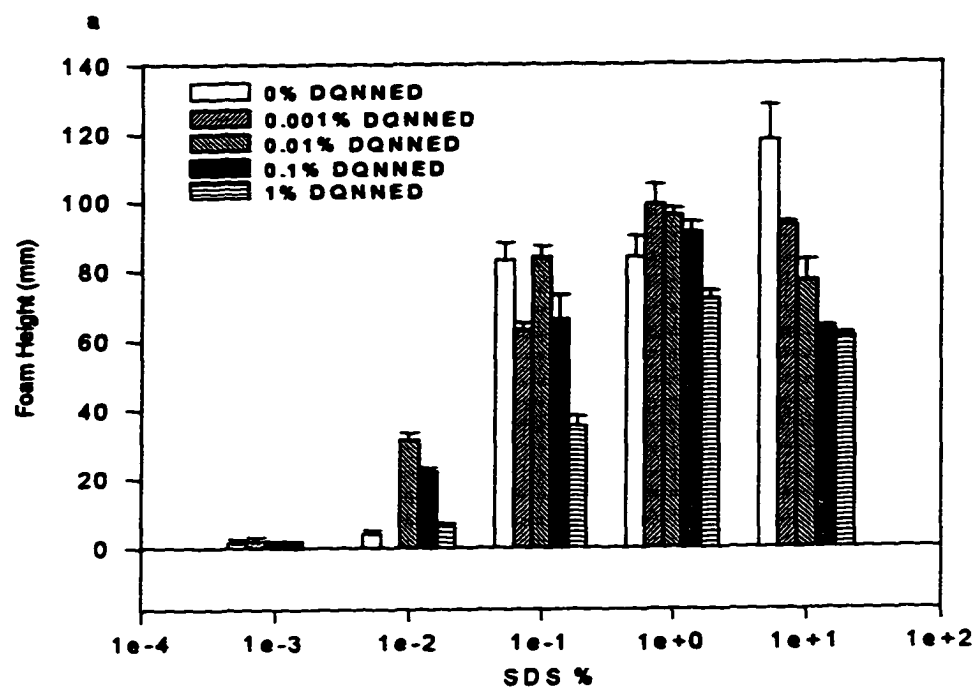
The effect of DQNNED on foam stability was studied as previously described for Polyquaternium 10 and MQNNED. The initial overall maxima in foam height was observed for solutions containing 0.001 - 1% DQNNED and 1% SDS, similar to the other two polymers (Figure 9.9a). The normalized foam height data shows that maximal foaming occurs at 0.01% DQNNED and 0.01% SDS (Figure 9.10). Addition of 0.01% DQNNED produced the greatest increase in initial foam height. However, the foamability of solutions containing DQNNED was significantly less than for the same solutions containing MQNNED.

After 24 hours, the solution containing 0.01% DQNNED and 0.1% SDS contained the maximum amount of foam (Figure 9.9a-e). This result is similar to the result produced by addition of MQNNED. The final foam height remaining after 24 hours for this solution is approximately half that of the amount remaining in the same solution containing 0.01% MQNNED. Therefore, a polymer containing two positive charges closely associated with the polymer backbone per cellulose unit does not improve foaming as well as its monoquaternary analog.

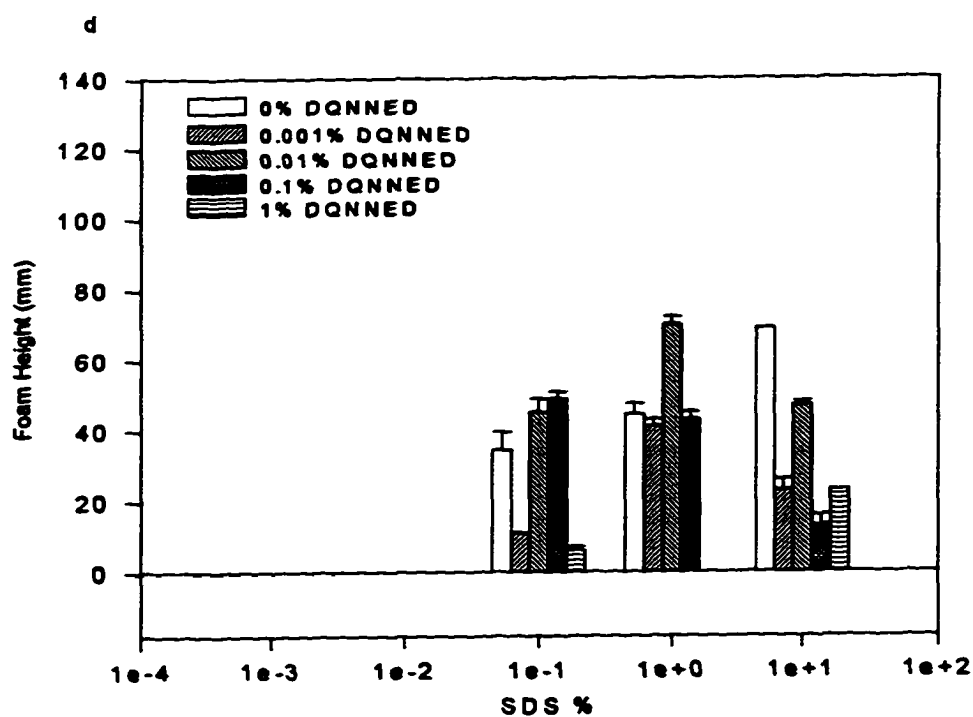
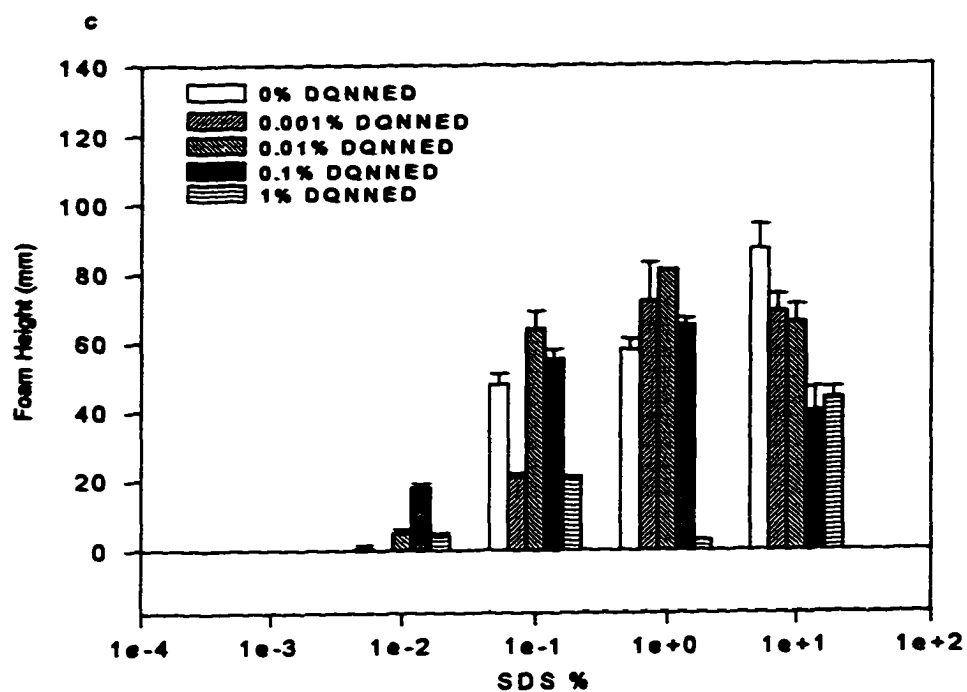
Analysis of half-life data (Table 9.4) indicates that foam stability is greatest for the solution containing 0.01% DQNNED and 0.1% SDS. The half-life was 33.54 hours (1 day, 9 hours, 32 minutes). This result is similar to the results for MQNNED; however, the same solution containing MQNNED had a half-life 4.7 times greater than

Figure 9.9: Determination of Foam Height for DQNNED and SDS

- (a) initial
- (b) 30 minutes elapsed
- (c) 1 hour elapsed
- (d) 6 hours elapsed
- (e) 24 hours elapsed



(Figure continued)



(Figure continued)

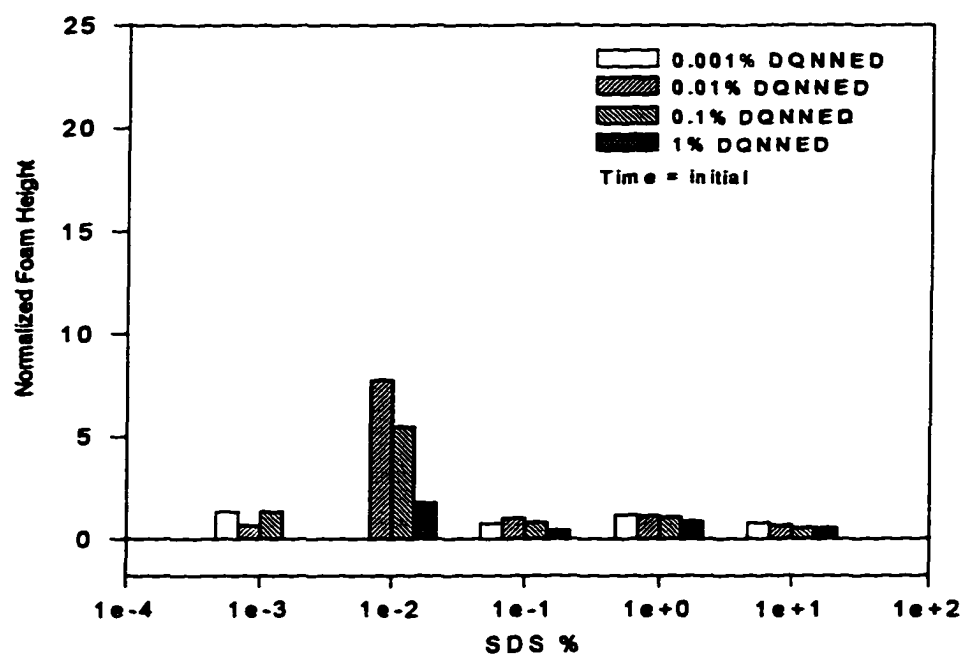
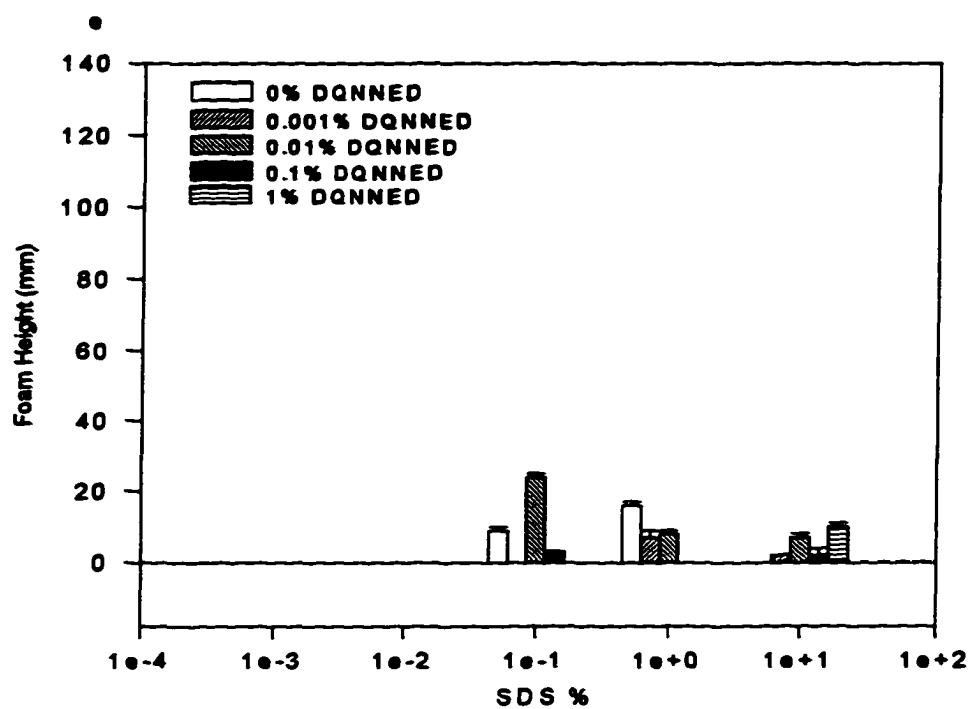


Figure 9.10: Foam Height Normalized for Amount of Foam Produced by SDS Alone.

Table 9.4 : Half-lives, Surface Tension and Specific Viscosity for Systems of DQNNED and SDS

| DQNNED % | SDS % | slope = k sec⁻¹ | time sec | hours | γ @ 22°C mN / m | η specific |
|---------------------------|------------------------|---|---------------------------|--------------|----------------------------------|-------------------|
| 0.001 | 0.001 | N / A | < 1.80 e3 | < 0.5 | 73.15 | -0.049 |
| 0.01 | 0.001 | N / A | < 1.80 e3 | < 0.5 | 72.68 | 0.020 |
| 0.1 | 0.001 | N / A | < 1.80 e3 | < 0.5 | 40.37 | 0.319 |
| 1 | 0.001 | N / A | N / A | N / A | 57.98 | 2.440 |
| 0.001 | 0.01 | N / A | N / A | N / A | 52.20 | -0.049 |
| 0.01 | 0.01 | -2.20 e-4 | 3.15 e3 | 0.88 | 61.31 | -0.030 |
| 0.1 | 0.01 | -2.00 e-5 | 3.46 e4 | 9.63 | 44.48 | 0.403 |
| 1 | 0.01 | -7.00 e-5 | 9.90 e3 | 2.75 | 55.45 | 2.850 |
| 0.001 | 0.1 | -3.00 e-5 | 2.31 e4 | 6.42 | 31.24 | -0.049 |
| 0.01 | 0.1 | -5.74 e-6 | 1.20 e5 | 33.54 | 34.20 | N / A * |
| 0.1 | 0.1 | -2.00 e-5 | 3.46 e4 | 9.63 | 43.77 | 0.028 |
| 1 | 0.1 | -3.00 e-5 | 2.31 e4 | 6.42 | N / A | N / A * |
| 0.001 | 1 | -1.00 e-5 | 6.93 e4 | 19.25 | 36.83 | 0.013 |
| 0.01 | 1 | -1.00 e-5 | 6.93 e4 | 19.25 | 38.26 | 0.058 |
| 0.1 | 1 | -1.00 e-5 | 6.93 e4 | 19.25 | 36.29 | 0.086 |
| 1 | 1 | -3.80 e-5 | 1.82 e3 | 0.51 | 34.70 | 3.710 |
| 0.001 | 10 | -2.00 e-5 | 3.46 e4 | 9.63 | 33.23 | 0.950 |
| 0.01 | 10 | -1.00 e-5 | 6.93 e4 | 19.25 | 34.27 | 1.030 |
| 0.1 | 10 | -2.00 e-5 | 3.46 e4 | 9.63 | 33.75 | 1.176 |
| 1 | 10 | -8.38 e-6 | 8.27 e4 | 22.98 | 32.78 | 5.580 |

N/A = not applicable

N/A * this solution contained precipitated material and could not be determined by Ubbelohde

the half-life for DQNNED. This result indicates that the second positive charge on the graft does not contribute to increased foam stability. Solutions containing the lowest concentrations of SDS exhibited half-lives of less than 30 minutes. Additionally, two solutions did not foam.

For all the solutions studied, surface tension decreased and specific viscosity increased as the concentration of DQNNED was increased. The solutions nearest the plait point for the system DQNNED / SDS / water (Figure 9.11), those containing 0.01 or 0.1% SDS, exhibited an increase in foam stability. This result agrees with the work of Ross and Nishioka¹⁸¹⁻¹⁸⁴ which indicates that maximal foaminess is reached near the plait point composition in a three component system. This result is true regardless of the rigidity of the graft on the cellulose backbone or the number of quaternary nitrogens located on the graft.

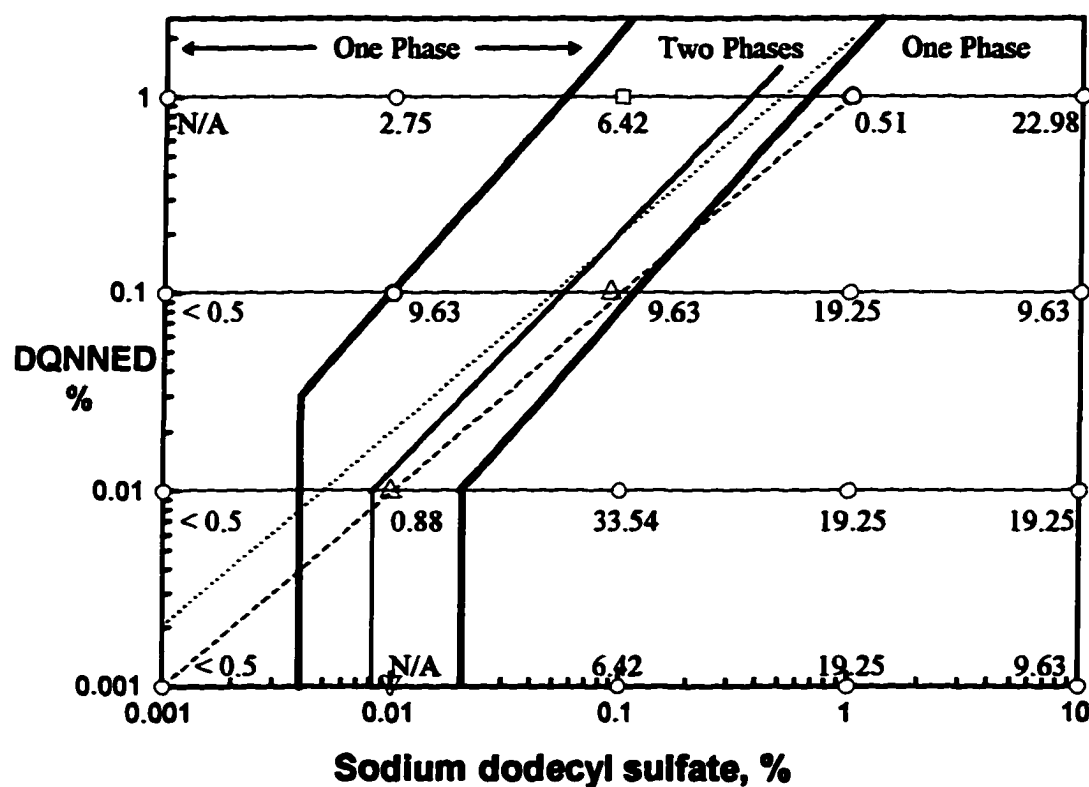


Figure 9.11: Phase Diagram and Foam Half-life for SDS / Water / DQNNED.

Symbols indicate: O clear solution; ● precipitate; ∇ slight precipitate; Δ hazy solution; □ gel; - - - - - Theoretical charge neutralization for 1 SDS; Theoretical charge neutralization for 2 SDS; and ——— Maximum precipitate observed.

9.7.4 Comparison of Effects on Foam Stability as a Result of Polymer Structure

The results of foamability are shown in Table 9.5 for the three polymers studied. The system containing Polyquaternium 10 which is quaternized hydroxyethyl cellulose requires more polymer to produce maximal foamability of SDS than does either MQNNED or DQNNED. Although these solutions produced the maximum initial foam height, they were not the most stable over time (Table 9.6). Solutions exhibiting the largest half-life contained 10 times more SDS than those producing maximal initial foam height. Both MQNNED and DQNNED exhibited the greatest half-life at the same concentrations of polymer and SDS. The half-life for DQNNED was 4.7 times shorter than the similar MQNNED system. This indicates that the second cationic charge per graft reduces foam stability.

Table 9.5 : Maximal Normalized Foam Height (Foamability)

| Polymer | % Polymer / % SDS | Normalized Foam Height |
|-------------------|-------------------|------------------------|
| Polyquaternium 10 | 0.1% / 0.001 % | 20.7 |
| MQNNED | 0.1% / 0.01% | 15.8 |
| DQNNED | 0.01% / 0.01% | 7.8 |

Table 9.6 : Half-life, Specific Viscosity and Surface Tension for Most Stable Solution

| Polymer | Polymer % | SDS % | $t_{1/2}$ (hours) | γ @ 22°C (mN / m) | η specific |
|-------------------|-----------|-------|-------------------|--------------------------|-----------------|
| Polyquaternium 10 | 0.1 | 0.01 | 116.23 | 46.36 | 1.840 |
| MQNNED | 0.01 | 0.1 | 156.54 | 31.13 | 0.020 |
| DQNNED | 0.01 | 0.1 | 33.54 | 34.20 | N / A |

N / A = not applicable as the solution contained precipitated material.

9.8 CONCLUSIONS

The system containing Polyquaternium 10 requires more polymer to produce maximal foamability of SDS than does either MQNNED or DQNNED. Therefore, polymers containing a cationic charge closely associated to the polymer backbone will show improvements in initial foamability of SDS solutions. Although these solutions produce the maximum initial foam height, they are not the most stable over time. A greater amount of SDS is required for the solutions to produce a stable foam. At the higher concentration of SDS, polymers containing a single cationic charge closely associated to the polymer backbone exhibit the most stable foams as the second cationic charge per graft appears to reduce foam stability.

CHAPTER 10: ANTIMICROBIAL ACTION OF QUATERNARY POLYMERS

10.1 INTRODUCTION

10.1.1 Quaternary Ammonium Compounds

The quaternary nitrogen functional group is an essential component in many biologically active compounds.¹⁸⁵ This moiety, found in B vitamins and enzymes, plays an important role in living processes.¹⁸⁶ Four types of physiologic actions are associated with compounds containing quaternary nitrogens: curare like, muscarinic - nicotinic action, ganglia blocking and neuromuscular blockade.¹⁸⁶

Quaternary ammonium compounds (quats) are products of a nucleophilic substitution reaction of alkyl halides with tertiary amines. They have the general formula (Figure 10.1) where R₁, R₂, R₃, and R₄ are alkyl groups, and X is an anion, usually a halogen.

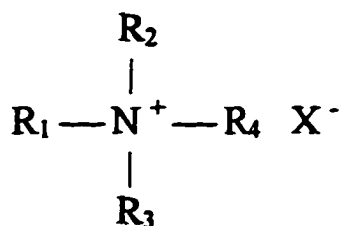


Figure 10.1: Structure of a Quaternary Ammonium Compound.

Jacobs and Heidelberger were the first researchers to examine the structure, preparation and antimicrobial activity of quats, particularly hexamethylenetetrammonium salts.^{187,188} Later, Browning *et al* described the antiseptic activity of quaternary derivatives of pyridine, quinoline and other ring structures.^{189,190} In 1935, Domagk¹⁹¹ disclosed

antibacterial activity of long-chain quaternary ammonium salts. Therefore, the increased activity that occurs when a quaternary nitrogen is attached to a large aliphatic residue was established.

Since these early reports, six generations of quaternary nitrogen compounds have been developed. These generations are: 1.) standard benzalkonium chloride; 2.) substituted benzalkonium compounds; 3.) dual quats; 4.) twin chain quats; 5.) 60/40 blends of the twin chain quats; and 6.) quaternary ammonium polymers.¹⁸⁵

Quaternary compounds are examples of surface active agents that in themselves possess antimicrobial activity.⁶⁷ These compounds function by adsorbing on the bacterial cell surface. They bring about destruction by increasing the permeability of the lipid cell membrane. Death occurs through loss of essential cell materials. Both gram positive and gram negative bacteria are susceptible to quats.^{67,81}

Quaternary compounds are used in water treatment, as liquid laundry detergent sanitizers, in preoperative patient treatment for surgery and disinfection of surgical instruments. In the cosmetics and pharmaceutical industry, they are used as preservatives for consumer products. They are disinfectants in the treatment of food contact surfaces, and are incorporated into latex paints as fungistats.

10.1.2 Quaternary Ammonium Polymers

There are different classes of synthetic and modified natural polymers exhibiting antimicrobial activity.¹⁹² In these polymers, the active moiety can be part of the main polymer structure or chemically bonded to the polymer and released through hydrolysis. Polymers may contain the active site as part of the backbone, i.e. biguanides, (Figure 10.2) or pendant away from the backbone chain, i.e. poly(ionenes) (Figure 10.3).

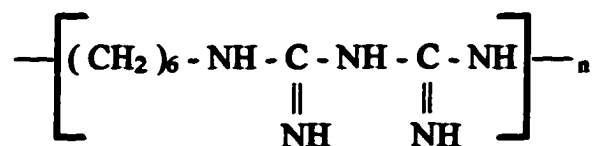


Figure 10.2: Structure of Bis(biguanide).

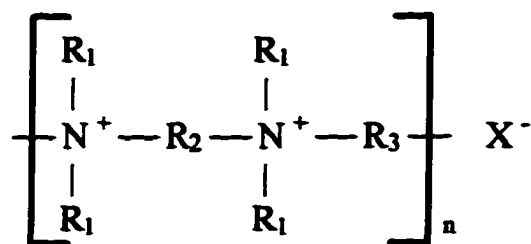


Figure 10.3: General Structure of a Poly(ionene) where R_1 , R_2 , and R_3 are alkyl groups, and X is an anion, usually a halogen.

Biocidal polymers have been divided into five classes: quaternary ammonium polymers, phosphonium polymers, halogenated polystyrene-divinylbenzene sulfonamides, N-halamine polymers and others.¹⁹³ These polymers have numerous potential applications in water treatment, health care and hygienic applications, coatings, textiles, disinfection of air and gas, and as preservatives.

Quaternary polymers are generally more active than their corresponding monomers, particularly against gram-positive bacteria.^{185,194} This effect is due to adsorption of the polymers onto the bacterial cell surface and cytoplasmic membrane with subsequent disruption of its integrity. Antimicrobial activity increases as the content of the quaternary ammonium moiety increases.¹⁸⁵ However, quaternary

polymers have the disadvantage that they may diffuse through the cell wall, particularly with gram negative bacteria.

Ikeda and Tazuke ¹⁹⁴ have demonstrated the molecular weight dependence on antimicrobial action of polymers. These researchers have shown that an optimal molecular weight range exists. Kourai *et al.* ¹⁹⁵ have studied the structure - activity relationships for N-laurylpyridinium iodides. They found that electron releasing groups on the pyridine nucleus, such as amino or methyl, increased activity while electron attracting groups, such as carbonyl or carbamoyl, decreased activity. The activity was linearly dependent on the electron density of the quaternary ammonium moiety.

10.1.3 Mechanism of Action

The mechanism of action for quaternary polymers has not been extensively studied.^{192,193} However, polyquats are anticipated to interact with bacteria in a similar manner as non-polymeric quats and other cationic compounds.^{185,192} The mechanism of action is adsorption of the polyquat on the bacterial cell surface (Figure 10.4), diffusion through the cell wall and binding to the cytoplasmic membrane. Adsorption onto the bacterial surface interferes with permeability and transport across the cell membrane. This interference disrupts the cytoplasmic membrane and causes leakage of potassium ions and other low molecular weight cytoplasmic components. Leakage of macrocomponents of the cell and subsequent precipitation of the cell components follows the death of the microorganism. Polyquats having a higher molecular weight and multiple quaternary nitrogens exhibit increased activity as the charge density increases the attraction to the negatively charged cell membrane.¹⁹² Larger molecules are also thought to present a greater barrier to cell membrane transport processes.¹⁹²

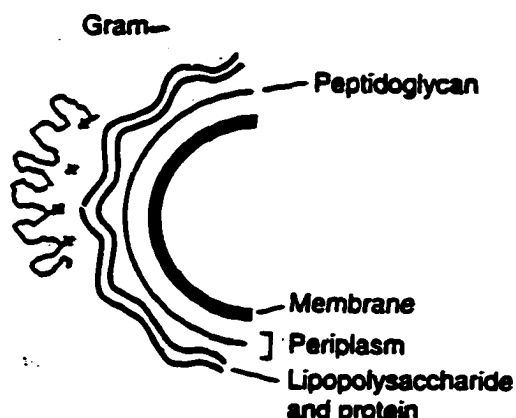


Figure 10.4: Adsorption of a Polyquaternary Polymer on a Bacterial Cell.

10.1.4 Microbial Metabolism

Microorganisms grow and multiply by using the materials in their immediate environment as food sources. Bacteria and fungi are widely distributed in nature, and there are few places on or near the earth's surface free from contamination.⁸¹ Bacteria reside in many unlikely places, such as hot mineral springs, the effluents from gas works, stagnant salt lakes, and even in the essentially anhydrous environment of diesel fuel.⁸¹ Microorganisms can not survive in a sterile environment or the interior tissues of healthy plants and animals.

The microorganisms use enzymes to carry out reactions. Some basic reactions that may occur are : hydrolysis, dehydration, oxidation, reduction, decarboxylation, deamination, phosphorylation and dephosphorylation.⁸¹ In a product supporting the growth of different types of microorganisms, a variety of by-products will be produced and a certain amount of competition for essential nutrients will occur. The formation of acid end products and competition eventually limits bacterial growth. However, most

organisms are capable of carrying out neutralizing reactions and some degree of stabilization of the environment will be achieved. The growth rate and variety of reactions which occur indicate the need for preservation from microbial spoilage.

10.1.5 Preservation of Cosmetics

Preservation is defined as the act of retarding or preventing the deterioration of a product from the time of manufacture until the consumer completely uses all of the product in the container.¹⁹⁶ Many components used in the formulation of cosmetic products, such as fats, oils and surfactants, are susceptible to biological degradation by microorganisms.⁸¹ Preservatives are added to personal care products to inhibit the growth of bacteria, yeasts, or fungi, to increase the shelf life of the product, and to protect the consumer from infection.¹⁹⁷ It is recognized that cosmetic products more so than pharmaceutical products are liable to consumer abuse.^{81,197} Preservatives defend a product from microbial spoilage by killing or inhibiting the growth of microorganisms. The growth of the microorganism is prevented by depletion of water and nutrient sources, and disruption of the cell membrane of the microorganism.

Preservatives are employed to prevent or reduce the growth of microorganisms contaminating the product after its manufacture. Optimally, products that contain preservative agents should self-sterilize within 24 hours. Products containing less than 15% alcohol and which are in the pH range of 3 to 11 are subject to microbial spoilage. The amount of bacterial growth that will occur is determined by the pH, osmotic pressure, surface tension, and oxygen tension of the preservative system.⁸¹ Preservatives may fail when they are in insufficient concentration in the aqueous phase, interact with the ingredients of a formulation, or interact with the packaging components. A product

is well preserved if it withstands a laboratory challenge test and resists microbial insult during manufacture and consumer usage.

Normal healthy individuals have considerable resistance to infection by bacteria and fungi commonly found on their skin and in the environment.⁸¹ In susceptible individuals, such as infants, the very old, and those in ill health, there is an increased probability of infection. A product may contain a growing bacterial population even if there is no visible evidence. Such a product placed in intimate contact with the skin, particularly if broken or damaged, may give rise to infection.¹⁹⁸

Ideally, a preservative should be safe and effective in all types of products. The major requirements are: 1.) freedom from toxic, irritant, or sensitizing effects at use concentrations on skin, mucous membranes or in gastro-intestinal system; 2.) stable to heat and prolonged storage; 3.) compatibility with other formulation ingredients and packaging material; 4.) effective over a wide pH range; and have a suitable oil/water partition coefficient in order to have an effective concentration in the continuous phase.^{81,193,197,199} Unfortunately, no preservatives are available that exhibit all of the desired properties.¹⁹⁹ The extent of killing bacteria is governed by six factors: concentration of preservative, nature of bacterial cells and density, time of contact, temperature of the medium, pH and the presence of foreign matter.¹⁸⁵ Many types of preservatives have been used in cosmetic formulations (Table 10.1).^{81,200} Methylparaben (Methyl-4-hydroxybenzoate) is the most frequently used preservative.²⁰⁰ Mixtures of preservatives that are effective against different microorganisms are commonly used. Additionally, there are advantages to the use of combinations which act against not only a wide range of organisms but also act synergistically, such as imidazolinyl urea and the

parabens.⁸¹ Quats have been tested for irritation and sensitization properties, and, at concentrations below 0.1%, most appear to cause little or no irritation. However, most of the quats listed as preservatives are monographed only for use as conditioning agents in hair or skin products.¹⁸⁵

Table 10.1: Some Commonly Used Preservatives

| ACIDS | QUATS | PHENOLS |
|------------------------------------|-------------------------------------|---------------------------------|
| <i>p</i> -Hydroxybenzoic acid | Benzethonium chloride | Phenol |
| Benzoic acid | Benzalkonium chloride | Cresol |
| Sorbic acid | Cetyltrimethyl ammonium bromide | Chlorothymol |
| Dehydroacetic acid | Cetyl pyridinium chloride | Methylchlorothymol |
| Formic acid | Tetramethylthiuramdisulfide | Chlorobutanol |
| Salicylic acid | Imidazolidinyl urea | <i>o</i> -Phenylphenol |
| Boric acid | Dimethyldidodecyl ammonium chloride | Parachlormetacresol |
| Vanillic acid | | Parachlormetaxyleneol |
| | PARABENS | |
| <i>o,p</i> -Chlorobenzoic acid | Methyl <i>p</i> -hydroxybenzoate | β -Phenoxyethylalcohol |
| Propionic acid | Ethyl <i>p</i> -hydroxybenzoate | Dichlorophene |
| Sulfurous acid | Propyl <i>p</i> -hydroxybenzoate | Hexachlorophene |
| Trichlorophenylacetic acid | Butyl <i>p</i> -hydroxybenzoate | Vanillin |
| | Benzyl <i>p</i> -hydroxybenzoate | Ethyl vanillin |
| METAL CONTAINING | | |
| Sodium ethyl mercurithiosalicylate | | 2-Bromo-2-nitro-1,3-propanediol |
| Phenyl mercury acetate | ANILIDES | β -Phenoxypropylalcohol |
| | Tetrachlorsalicylanilide | |
| Phenyl mercury borate | Trichlorcarbanilide | Monomethylol dimethyl hydantoin |
| Phenyl mercury nitrate | Trichlorsalicylanilide | |

10.2 EXPERIMENTAL

10.2.1 Test Organisms

The strains of bacteria used in this study were received directly from the American Type Culture Collection (ATCC) and consisted of *Escherichia coli* (*E. coli*) 25922, *Staphylococcus aureus* (*S. aureus*) 29213 and *Pseudomonas aeruginosa* (*P. aeruginosa*) 27853. The cultures were stored frozen in a solution of nutrient broth and glycerol in order to prevent mutation. The cells were maintained by growth of a culture overnight in 5 ml of nutrient broth. The next morning, 1 ml of the culture was resuspended in 25 ml of nutrient broth at room temperature and placed in a shaker-incubator for 4 hours at 150 rpm and 37 °C to ensure a cell density of at least 10^8 cells / ml in mid-logarithmic growth phase. The optical density (OD) of the cell solution was measured at 600 nm using a spectrophotometer. The suspensions were diluted with nutrient broth until the OD read 0.20 ± 0.01 for *E. coli* or *P. aeruginosa* and 0.40 ± 0.01 for *S. aureus*. These OD readings correspond to concentrations of 10^8 bacterial cells / ml of nutrient broth. Aerobic plate counts (APCs) were performed in order to determine the size of each inoculum.

10.2.2 Preparation of Nutrient Broth and Agar Plates

10.2.2.1 Nutrient Broth

Nutrient broth was prepared by dissolving 8 g of soy trypsin digest protein per liter of deionized water. The pH of the solution was adjusted to 7.2 ± 0.2 with 1 M sodium hydroxide. The nutrient broth was autoclaved prior to use.

10.2.2.2 Agar Plates

Agar was prepared by dissolving 40 g of Tryptic Soy Agar per liter of deionized water. The pH of the solution was adjusted to 7.2 ± 0.2 with 1 M sodium hydroxide. The agar was autoclaved prior to use. Agar plates were prepared by pouring the hot autoclaved agar into gamma irradiated petri dishes. The dry agar plates were stored in a refrigerator prior to use in tests.

10.2.3 Test Solutions

Aqueous solutions of 0.2% (w/v) Methyl-4-hydroxybenzoate (methylparaben), 0.2% (w/v) 3-trimethylammonium-2-hydroxypropyl-N,N-dimethylammoniummethyl carbamoylmethyl cellulose chloride (DQNNED), 0.2% (w/v) methylparaben and 0.2% (w/v) DQNNED, and 0.002% (w/v) 3-trimethylammonium-2-hydroxypropyl-N-chitosan (CHI-Q188) were prepared with sterile deionized water. The pH of the solutions was adjusted to 7.0 ± 0.2 with 1 M sodium hydroxide. Sterile, deionized water was used as a control for the experiments. Solutions were stored at room temperature prior to use.

10.2.4 Test Methods

10.2.4.1 Minimum Inhibitory Concentration Test

The test used in this study was the Minimum Inhibitory Concentration Test (MIC). This is a general test that indicates the minimum concentration necessary to inhibit the growth of a population of microorganisms. The pathogen, *E. coli*, *S. aureus* or *P. aeruginosa*, is added to a small well containing the polymer of interest, phosphate buffer, and nutrient broth.

A range of eight concentrations may be tested at once so the minimum concentration at which the polymer will prevent growth can be determined. A

concentration of 10^4 bacterial cells / ml was studied in each test. The polymer concentration tested ranged from approximately 1600 μg / ml to 2 μg / ml. For each set of tests there was a cell control and a polymer control. The well plates were incubated for 18 to 24 hours at 37 °C, the ideal temperature for microbial growth.

The cell well where the concentration of the polymer was effective at inhibiting growth will appear clear. The concentrations of the polymer at which growth occurs will appear cloudy (turbid) from the large population of cells that have grown. The experiment was repeated several times, as indicated, to obtain a sufficient average value for the MIC. Cell wells were judged visually for clarity of the solutions.

10.2.4.2 Sterilization Times

A modified preservative efficacy test (PET) ²⁰¹ was used to determine sterilization times (STs) for the test organisms in aqueous samples. The inocula were prepared as described and added to buffered solutions of methylparaben, DQNNED, methylparaben and DQNNED, and CHI-Q188. The contents of test tubes were mixed using a Vortex Genie mixer. 100 μl of the room temperature samples were spread on agar plates at time intervals of 0 to 48 hours. Agar plates were incubated for 18 to 24 hours at 37 °C. The agar plates were examined for growth of the test organisms, and the ST was determined to be the time at which test organisms were not recovered from the solution. When no endpoint was reached in the ST experiments, because the bacteria were still alive at 48 hours, the minimum possible ST (MPST) was used. The MPST is defined as a time longer than the last time at which test organisms were recovered.²⁰¹

10.3 RESULTS AND DISCUSSION

10.3.1 Minimum Inhibitory Concentration

In this experiment, the antimicrobial activity of two polymers with quaternary ammonium groups located on polysaccharides *versus* methylparaben was studied using the MIC test. Methylparaben (Figure 10.5) was chosen as a comparison with the quaternary polysaccharide polymers as it is the most frequently used cosmetic preservative.

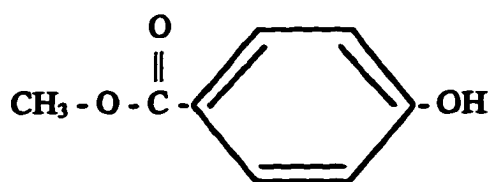
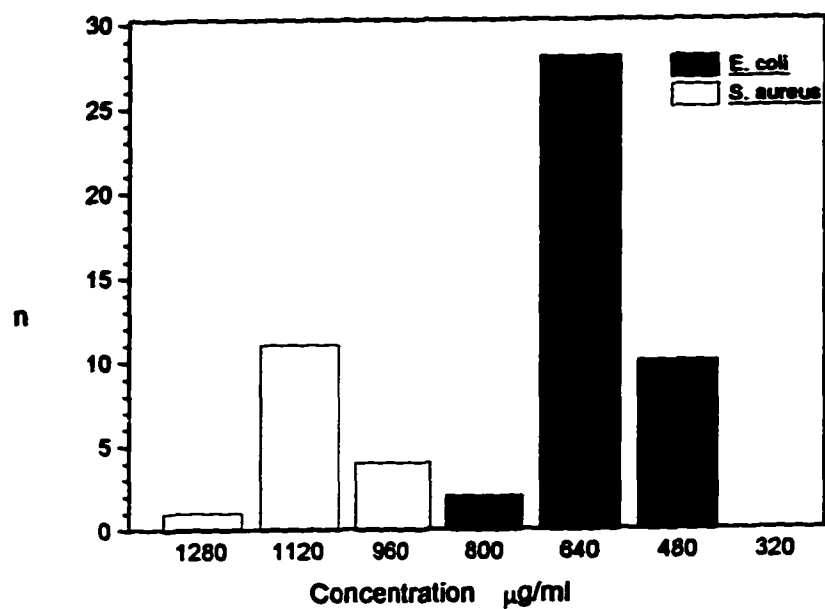


Figure 10.5: The Structure of Methylparaben.

The MIC results for methylparaben and the polymers tested are shown. The MIC for methylparaben was found to be 640, 800 and 1120 $\mu\text{g} / \text{ml}$ for *E. coli*, *P. aeruginosa* and *S. aureus*, respectively (Figures 10.6). *S. aureus* which is a gram positive bacteria required twice as much methylparaben to inhibit growth as *E. coli* or *P. aeruginosa* which are gram negative. The MIC of the first polysaccharide tested, DQNNED, which contains a quaternary nitrogen and carbamoyl group was found to be 480, 480 and 1760 $\mu\text{g} / \text{ml}$ for *E. coli*, *P. aeruginosa* and *S. aureus*, respectively (Figure 10.7). This polymer inhibited growth as well as methylparaben. In the case of *S. aureus*, approximately 3.6 times more DQNNED was required to inhibit growth as *E. coli* or *P. aeruginosa*.

(a)



(b)

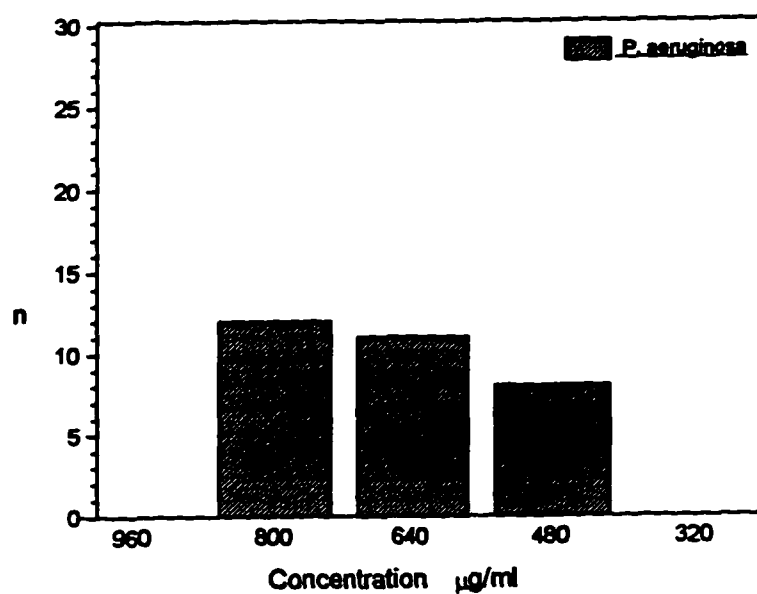
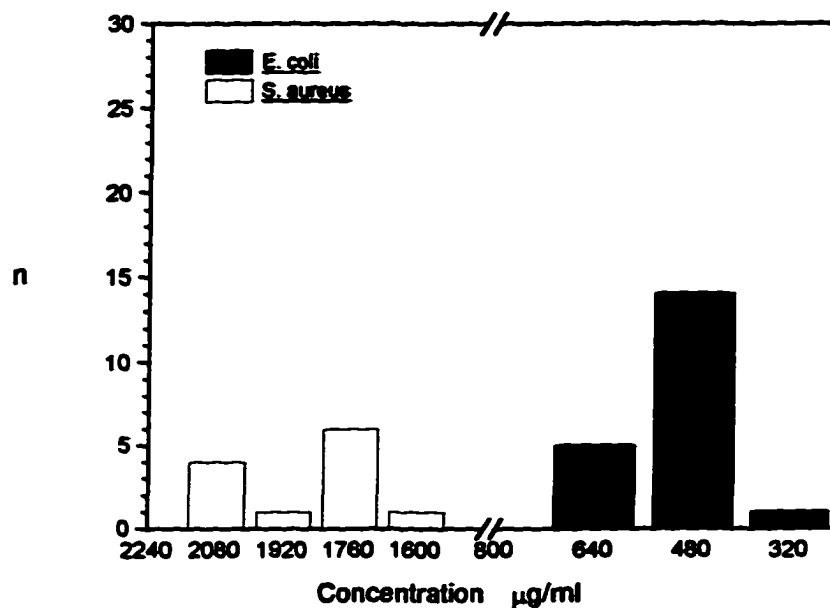


Figure 10.6: MIC Test Results for Methylparaben (a) *E. coli* and *S. aureus*; (b) *P. aeruginosa*.; n is the number of MIC tests.

(a)



(b)

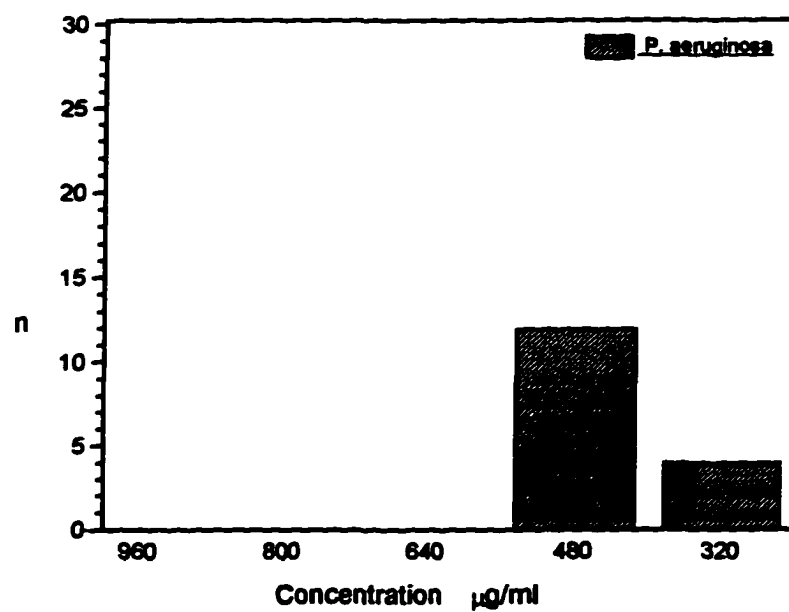


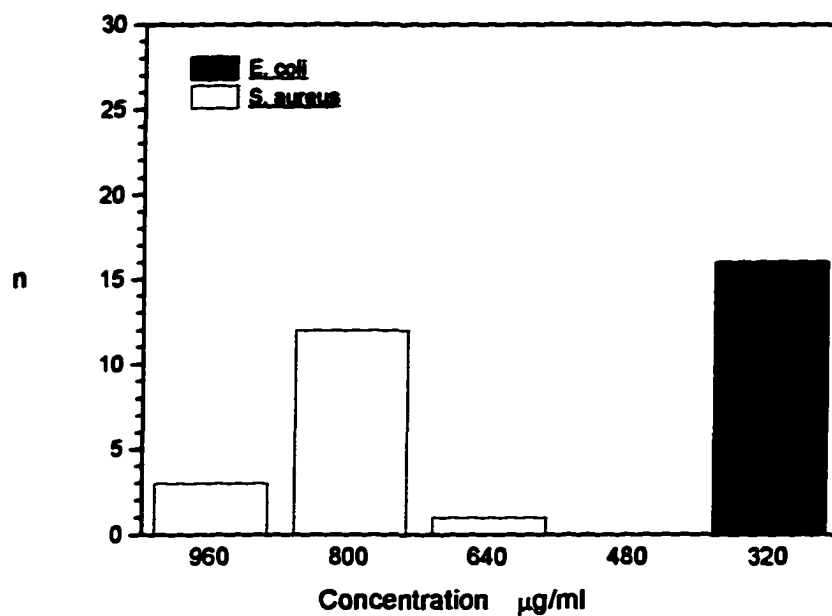
Figure 10.7: MIC Test Results for DQNNED; (a) *E. coli* and *S. aureus*; (b) *P. aeruginosa*.; n is the number of MIC tests.

The MIC of the combination of DQNNED and methylparaben was found to be 320, 160 and 800 $\mu\text{g} / \text{ml}$ of each of the compounds for the inhibition of *E. coli*, *P. aeruginosa* and *S. aureus*, respectively (Figure 10.8). This effect of the combination of DQNNED and methylparaben on bacterial growth appears to be additive rather than synergistic. This result shows that a quaternary polymer may be incorporated into a product and contribute to the preservation of the product. Therefore, quaternary polymers may have dual roles in formulation as rheology modifiers and preservatives.

The MIC of the second type of polysaccharide containing a quaternary nitrogen, CHI-Q188, was found to be 16 $\mu\text{g} / \text{ml}$ for all three bacteria tested, *E. coli*, *P. aeruginosa* and *S. aureus* (Figure 10.9). This polymer is 40 times more effective against *E. coli* than methylparaben and 30 times more effective than DQNNED. CHI-Q188 is 50 times more effective against *P. aeruginosa* than methylparaben and 30 times more effective than DQNNED. Similarly, CHI-Q188 is 70 times more effective against *S. aureus* than methylparaben and 110 times more effective than DQNNED.

The effectiveness of CHI-Q188 against both types of bacteria may be a result of the chitosan backbone itself. The lower molecular weight of this derivative in comparison with the cellulose derivative may allow more polymer molecules to adsorb on each bacterial cell thereby enhancing the activity. DQNNED, which has a carbamoyl moiety adjacent to the quaternary nitrogen, may have a lower activity due to the presence of this electron withdrawing group. It has been shown that electron withdrawing groups, such as carbonyl and carbamoyl, decrease the activity of certain antimicrobial agents.¹⁹⁵

(a)



(b)

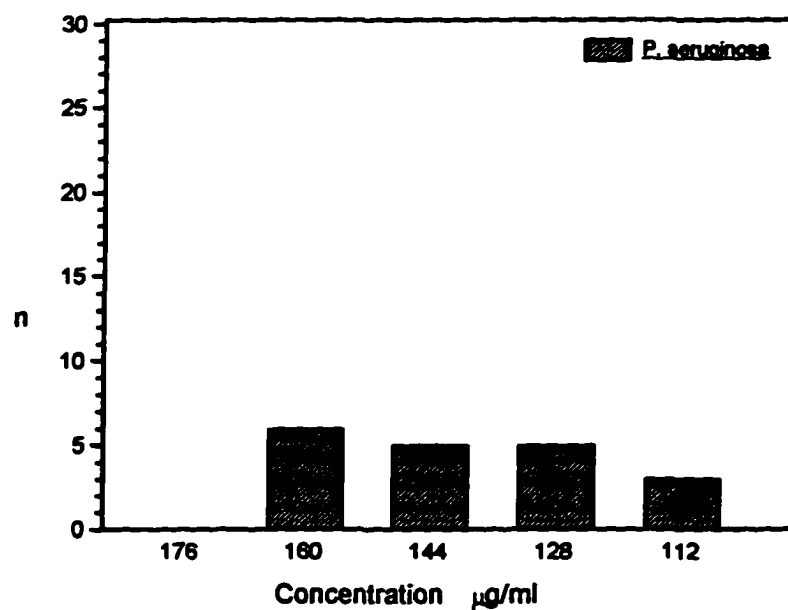
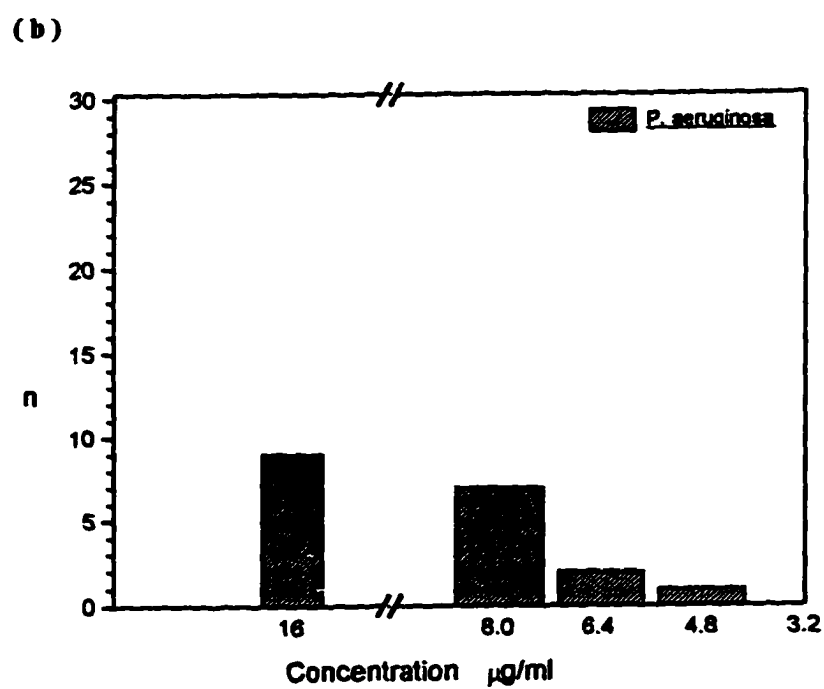
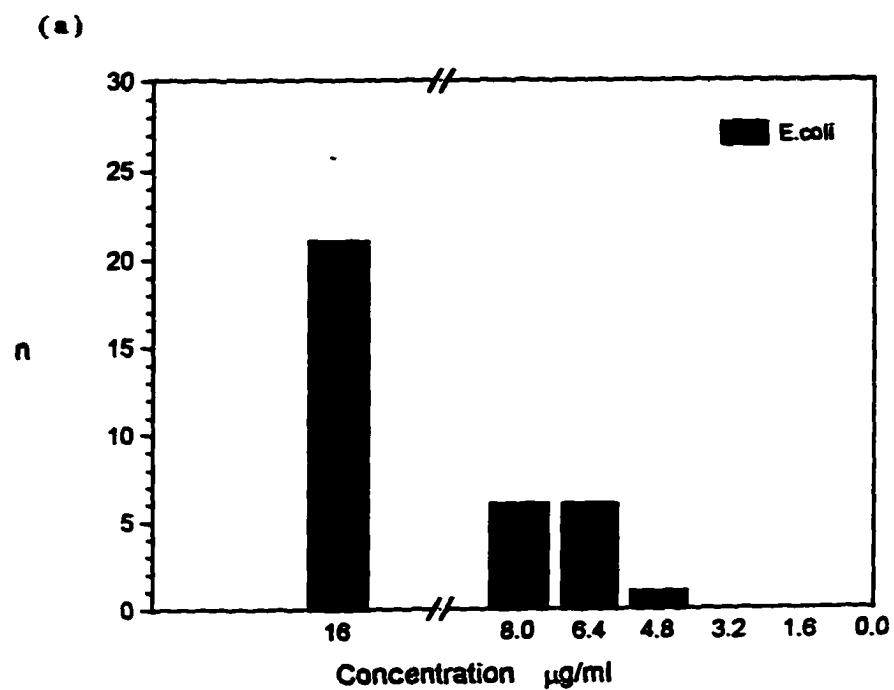
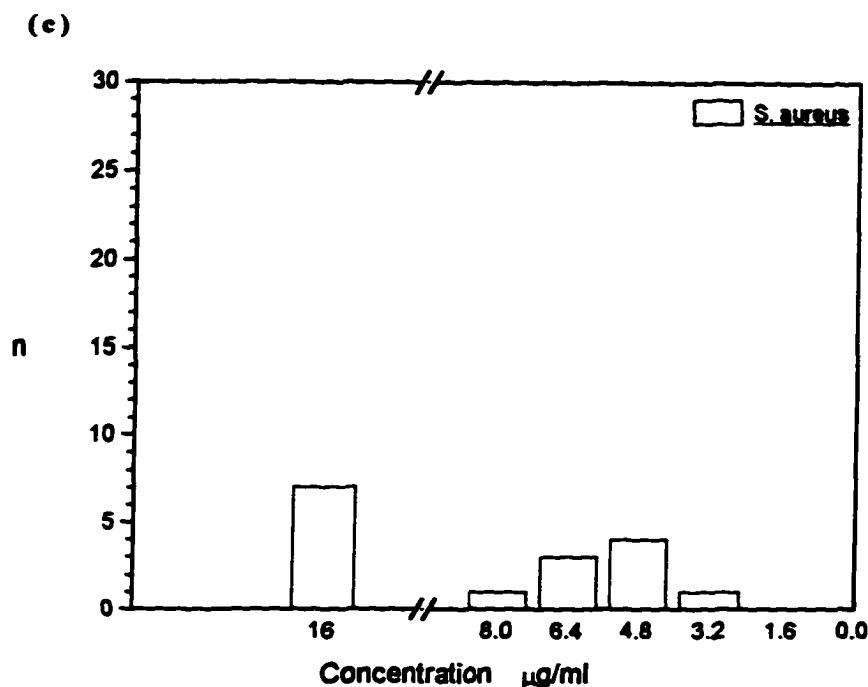


Figure 10.8: MIC Test Results for Methylparaben and DQNNED; (a) *E. coli* and *S. aureus*; (b) *P. aeruginosa*.; n is the number of MIC tests.

Figure 10.9: MIC Test Results for CHI-Q188:
(a) *E. coli*;
(b) *P. aeruginosa*; and
(c) *S. aureus*.
n is the number of MIC tests.



(Figure continued)



The unquaternized aminoalkylcarbamoyl cellulose and hydroxypropylchitosan derivatives did not exhibit antimicrobial activity. This result indicates that the antimicrobial activity is a result of the quaternary ammonium groups.

10.3.2 Sterilization Times

Sterilization times of *E. coli* and *S. aureus* in solutions of methylparaben, DQNNED, and a mixture of DQNNED and methylparaben were determined (Table 10.2). The 2000 µg / ml methylparaben solution was not rapidly bactericidal as test organisms were recovered at 48 hours. This result agrees with the results of Orth et al.²⁰¹ for ST of *E. coli* and *S. aureus* by a 0.2% aqueous solution of methylparaben. Neither the solution of DQNNED nor the mixture of DQNNED and methylparaben were rapidly bactericidal. Test organisms were again recovered in the solutions at 48 hours. This

Table 10.2: Determination of Sterilization Times of Bacterial Species in Methylparaben, DQNNED, and DQNNED and Methylparaben.

| 2000 µg / ml Methylparaben solutions | | | | | | | | |
|---|------|------|------|------|-------|-------|----|------|
| Test organism | 0 hr | 1 hr | 2 hr | 4 hr | 24 hr | 48 hr | ST | MPST |
| <i>E. coli</i> 25922 | + | + | + | + | + | +[12] | – | >48 |
| <i>S. aureus</i> 29213 | + | + | + | + | +[61] | +[28] | – | >48 |
| 2000 µg / ml DQNNED solutions | | | | | | | | |
| Test organism | 0 hr | 1 hr | 2 hr | 4 hr | 24 hr | 48 hr | ST | MPST |
| <i>E. coli</i> 25922 | + | + | + | + | + | + | – | >48 |
| <i>S. aureus</i> 29213 | + | + | + | + | +[84] | + | – | >48 |
| 2000 µg / ml Methylparaben and 2000 µg / ml DQNNED solutions | | | | | | | | |
| Test organism | 0 hr | 1 hr | 2 hr | 4 hr | 24 hr | 48 hr | ST | MPST |
| <i>E. coli</i> 25922 | + | + | + | + | + | +[24] | – | >48 |
| <i>S. aureus</i> 29213 | + | + | + | + | + | + | – | >48 |
| Sterile, Deionized Water (control) | | | | | | | | |
| Test organism | 0 hr | 1 hr | 2 hr | 4 hr | 24 hr | 48 hr | ST | MPST |
| <i>E. coli</i> 25922 | + | + | + | + | + | + | – | >48 |
| <i>S. aureus</i> 29213 | + | + | + | + | + | + | – | >48 |

Explanation of symbols: +, growth on agar; –, no growth on agar; numbers in brackets (i.e., [12] and [24]) indicate the mean number of colonies growing on agar. ST, sterilization time in hours. MPST, minimum possible sterilization time in hours. All solutions tested contained 3.2 ml of the antimicrobial agent(s) of interest which gives a final concentration of 1600 µg/ml of antimicrobial agent, 0.4 ml of 50mM phosphate buffer which gives 5 mM phosphate buffer after dilution, and 0.4 ml of $1 \cdot 10^5$ bacterial colonies / ml which gives $1 \cdot 10^4$ colonies / ml after dilution. Tests were performed in triplicate using two different inocula; therefore, the data represent the mean values of six measurements. Aerobic plate counts (APC) of the inocula : *E. coli* 25922: $1 \cdot 10^4$ / ml, $3.2 \cdot 10^4$ / ml; *S. aureus* 29213 : $2.2 \cdot 10^4$ / ml, $2 \cdot 10^5$ / ml.

result is not surprising as quaternary polymers are known to be slow acting in killing microorganisms, and more biostatic than biocidal.¹⁹²

Sterilization times of *E. coli* and *S. aureus* in solutions of CHI-Q188 were determined (Table 10.3). The 20 µg / ml CHI-Q188 solution was rapidly bactericidal as test organisms were not recovered at 2 hours. Sterilization times were determined as 1.5 hours for *E. coli* and 30 minutes for *S. aureus*.

Table 10.3: Determination of Sterilization Times of Bacterial Species in CHI-Q188.

| 20 µg / ml CHI-Q188 solutions | | | | | | | | | |
|---|-------------|------------|-------------|------------|-------------|-------------|-------------|-----------|-------------|
| Test organism | 0 hr | 0.5 | 1 hr | 1.5 | 2 hr | 24hr | 48hr | ST | MPST |
| <i>E. coli</i> 25922 | + | +[10] | +[4] | – | – | N/A | N/A | 1.5 | – |
| <i>S. aureus</i> 29213 | +[13] | – | – | – | – | N/A | N/A | 0.5 | – |
| Sterile, Deionized Water (control) | | | | | | | | | |
| Test organism | 0 hr | 0.5 | 1 hr | 1.5 | 2 hr | 24hr | 48hr | ST | MPST |
| <i>E. coli</i> 25922 | + | + | + | + | + | + | + | – | >48 |
| <i>S. aureus</i> 29213 | + | + | + | + | + | + | + | – | >48 |

Explanation of symbols: +, growth on agar; –, no growth on agar; numbers in brackets (i.e., [10] and [4]) indicate the mean number of colonies growing on agar. ST, sterilization time in hours. MPST, minimum possible sterilization time in hours. N/A = not applicable as sterilization time was reached. All solutions tested contained 3.2 ml of the antimicrobial agent(s) of interest which gives a final concentration of 16 µg/ml of antimicrobial agent, 0.4 ml of 50mM phosphate buffer which gives 5 mM phosphate buffer after dilution, and 0.4 ml of $1 \cdot 10^5$ bacterial colonies / ml which gives $1 \cdot 10^4$ colonies / ml after dilution. Tests were performed in triplicate using two different inocula; therefore, the data represent the mean values of six measurements. Aerobic plate counts (APC) of the inocula : *E. coli* 25922 : $9.4 \cdot 10^3$ / ml, $3.2 \cdot 10^4$ / ml; *S. aureus* 29213 : $1.3 \cdot 10^4$ / ml, $2.2 \cdot 10^4$ / ml

10.4 CONCLUSIONS

The results of this study indicate the dual role that quaternary polymers may have in cosmetic products. They potentially may be used as thickeners or conditioners, and they may also exhibit antimicrobial activity in the preservation of the cosmetic products. The hydroxypropyl trimethylammonium chitosan chloride derivative appears to be bactericidal while the aminoalkylcarbamoyl cellulose derivative, DQNNED, appears to be only bacteriostatic. The exact difference between these two compounds is not completely understood at this point in time. However, we believe that it is either a molecular weight effect or the presence of the carbamoyl moiety in the DQNNED polymer. The chitosan derivative has a starting molecular weight of approximately 100,000 g/mol. Whereas the DQNNED has a starting molecular weight of 250,000 g/mol. This difference in molecular weight may allow a higher concentration of CHI-Q188 to be adsorbed on the cell membrane thereby increasing the efficacy of this compound. The carbamoyl moiety is electron attracting, therefore, it may reduce the efficacy of this derivative. More work in this area should be done in order to investigate the effects of molecular weight, degree of quaternization, and inclusion of electron releasing or attracting groups on the efficacy of these compounds.

**CHAPTER 11:
CHARACTERIZATION OF POLYMER DEPOSITS ON HUMAN
HAIR FIBERS**

11.1 INTRODUCTION

Deposition of compounds on human hair fibers is used extensively to modify the appearance, manageability and grooming style of hair.²⁰² Scanning Electron Microscopy (SEM), optical microscopy and fluorescence microscopy have been used to determine the film properties of resins, substantivity, and deposition of polymers on hair and wool fibers.^{57,60,202-204} Wettability scanning has been used to provide information on the surface coverage along the length of a fiber.²⁰² Microfluorometry has been used to scan the fluorescence intensity across or along a fiber to quantify the distribution of surface deposits on a relative basis.²⁰²

Typically, fluorescent probes have been used to qualitatively characterize the surface deposits on wool fibers²⁰²⁻²⁰⁴. Rothery and White²⁰³ have determined the presence and distribution of polymers on wool fibers by staining the polymer treated wool fibers with a fluorochrome and observing the fibers by optical microscopy under ultra violet light. Unfortunately, many of the fluorescent probes used have not been selective in binding to either the fiber or the polymer. We have used epifluorescence microscopy and SEM to determine the binding of our polymers to hair fibers. The fluorescent probe employed was *m*-dansylaminophenyl boronic acid (Dansyl-BA) which is covalently bonded to the polymer. Using this method, the fluorescence detected may be attributed to the polymer bound dye.

11.2 BINDING OF POLYMERS TO KERATIN

There are three factors that determine the binding of polymers to keratin: the affinity of the polymer for keratin, the binding interactions with the aqueous phase, and

the diffusibility of the ingredient into the hair.¹ Polymer-keratin affinity is influenced by polymer charge,²⁰⁵ molecular size,^{61,206} isoelectric point of the hair,³ pH of the surrounding medium,⁶¹ formulation composition,^{51,61,63} and ingredients attached to the fiber surface.¹ The hydrophilicity or hydrophobicity of the polymer affects the binding interactions with the aqueous phase. Diffusion into the fiber is controlled by the molecular size of the polymer, pH, reaction temperature, and the past history of the keratin.¹

Recently, it has been hypothesized that adsorption of a polymer onto keratin may proceed through two pathways: charge driven or hydrophobically driven.⁵⁵ Therefore, the adsorption process is viewed as a continuum between the two pathways as pH variation or structural modification of the polymer may change the mechanism of adsorption. At acid pH ($\text{pH} < 3.6$), the adsorption of cationic polymers is hydrophobically driven as the pH is near the isoelectric point of the hair. As pH increases above 3.6, the adsorption process becomes charge driven as the negative charge of the hair fiber increases with pH.

The types of bonding between polymers and keratin have been divided into three classes: primary valence bonds (ionic & covalent), polar interactions (hydrogen bonding) and van der Waals attractions.^{1,2} Cationic polymers, in particular, primarily bind to keratin through ionic bonds. This bonding is enhanced by van der Waals forces between the polymer and keratin.¹ The strength of van der Waals bonding may approach that of ionic bonding in polymers as the total strength of van der Waals bonding is the sum of individual interactions and thus increases with the number of repeat units in the polymer.

11.3 EXPERIMENTAL

11.3.1 Materials

The polymers were covalently labeled with *m*-dansylaminophenyl boronic acid (Dansyl-BA), catalog # D-2281, which was obtained from Molecular Probes (Eugene, Oregon). Dansyl-BA (Figure 11.1) is a unique probe that complexes with hydroxyl and amino groups to form cyclic complexes.²⁰⁷ In order to covalently bind the dye to the polymer, 0.5% aqueous solutions of the polymers were stirred in the dark over night with $1 \cdot 10^{-4}$ M Dansyl-BA. These solutions were then dialysed against distilled, deionized water to remove any unbound dye. Using this method, a minimal amount of the dye was covalently bound to the polymer. Any fluorescence detected could then be attributed to the polymer bound dye. Dansyl-BA ($\epsilon = 4.6 \cdot 10^3$) absorbs light at 337 nm and emits fluorescence at 517 nm in methanol. The fluorescence intensity and peak emission are environmentally sensitive²⁰⁸ and dependent upon the reaction product .

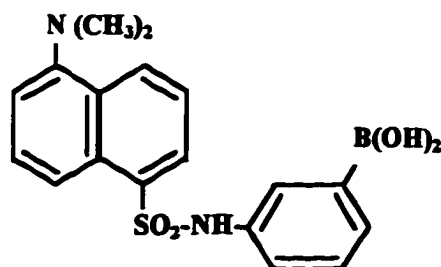


Figure 11.1: Structure of *m*-Dansylaminophenyl Boronic Acid.

Virgin hair was obtained from a male volunteer, age 33. Hair fibers were shampooed with a 1% solution of sodium dodecyl sulfate, rinsed with copious amounts of distilled, deionized water and dried in an oven at 60°C. The fibers were assembled

into 5 mg tresses and suspended into a solution. The tresses were treated for 5 minutes at room temperature in a gently stirred solution. The solutions contained either 0.4% polymer and $1 \cdot 10^{-4}$ M Dansyl-BA dye or 0.4% polymer, 1% SDS and $1 \cdot 10^{-4}$ M Dansyl-BA dye. After treatment, the fibers were rinsed with copious amounts of distilled, deionized water and dried in an oven at 60°C. A small portion of the fibers was removed for use in microscopy studies.

11.3.2 Equipment

A Nikon MICROPHOT-FXA equipped with a 40X objective and 10X oculars (total magnification of 400X) was used for epifluorescence microscopy. Photos were taken with TMAX 400 film, ASA 400. The photos were developed with TMAX developer in a ratio of 1:4. Digital images were also collected and saved as TIFF files which were viewed using Lviewpro software.

Samples were cut from the treated fibers and coated for Scanning Electron Microscopy (SEM). An Edwards S-150 Sputter Coater was used to coat the fiber with a gold-platinum (40/60) alloy. Approximately 200 Å of coating was applied per sample at 10 milliamps for 2 minutes in order to stabilize the samples. A Cambridge Stereoscan 260 Scanning Electron Microscope was used to produce photographic and digital images of the fiber samples. The SEM power was 9 kV, using a working distance of 10 -15 mm. The filament was fully saturated.

11.4 RESULTS AND DISCUSSION

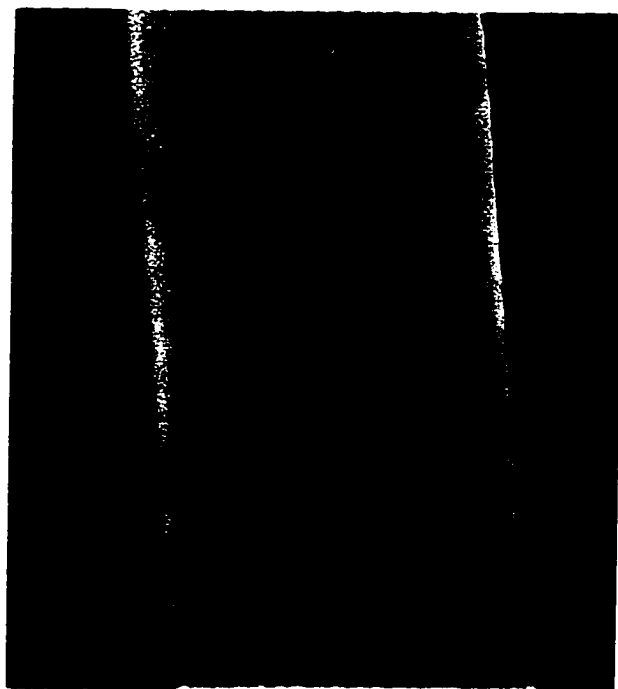
11.4.1 Epifluorescence Microscopy

The results of fluorescence microscopy are shown in Figure 11.2a-g. All the polymers and polymer - SDS solutions tested appear to uniformly coat the hair fibers as

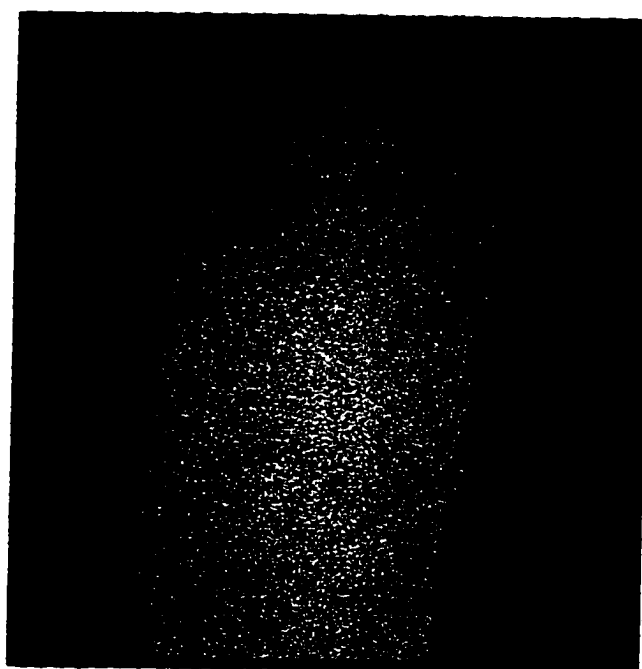
Figure 11.2: Characterization of the Deposition of Polymers on Hair Fibers Using Epifluorescence Microscopy

- (a) hair fiber treated with Dansyl-BA dye (control)**
- (b) hair fiber treated with Dansyl-BA labeled Polyquaternium 10 (0.4% polymer)**
- (c) hair fiber treated with Dansyl-BA labeled Polyquaternium 10 and SDS (0.4% polymer, 1% SDS)**
- (d) hair fiber treated with Dansyl-BA labeled MQNNED (0.4% polymer)**
- (e) hair fiber treated with Dansyl-BA labeled MQNNED and SDS (0.4% polymer, 1% SDS)**
- (f) hair fiber treated with Dansyl-BA labeled DQNNED (0.4% polymer)**
- (g) hair fiber treated with Dansyl-BA labeled DQNNED and SDS (0.4% polymer, 1% SDS)**

(a)

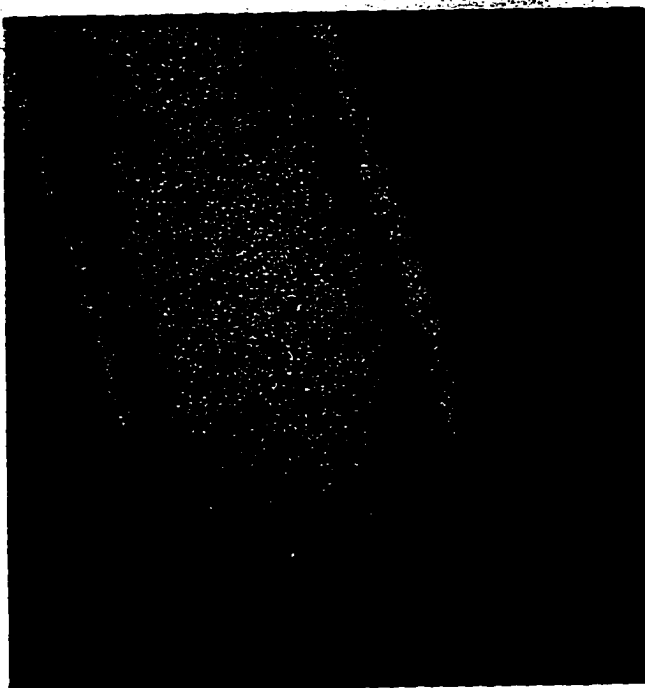


(b)

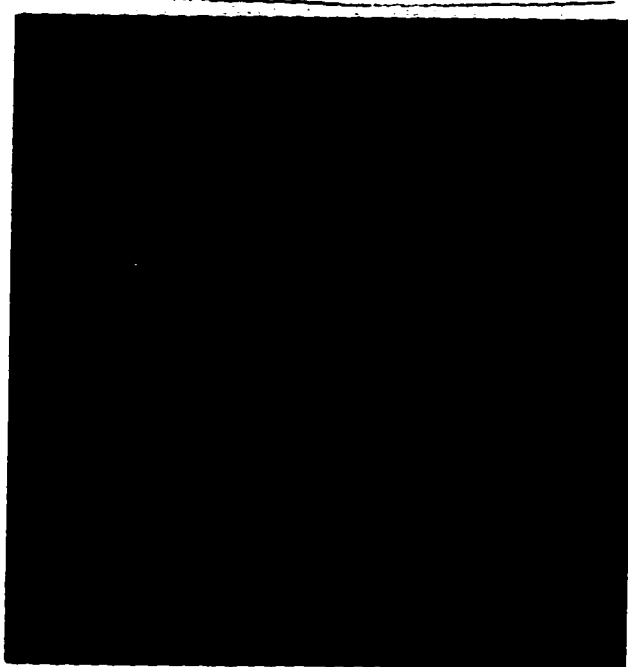


(Figure continued)

(c)

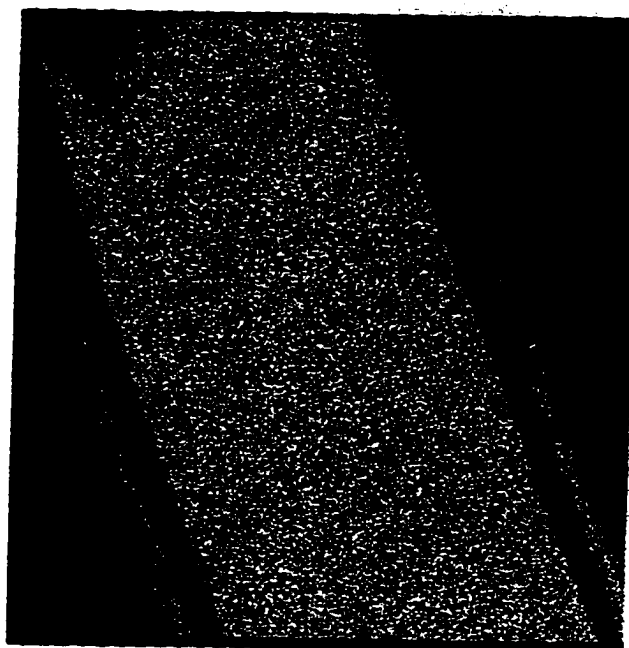


(d)



(Figure continued)

(e)



(f)



(Figure continued)

(g)



determined from the homogeneous fluorescence of the samples. Figure 11.2a shows the control which was a fiber treated with Dansyl-BA (10^4 M). The hair sample was determined to be undamaged as no sharp demarcation of the cuticle scales was observed. A sharp demarcation of the edged of cuticle scales in the form of a honeycomb pattern which is associated with fiber damage was reported by Weigmann *et al.*²⁰² The fluorescence intensity for fibers treated with solutions of polymer and SDS (Figure 11.2 c, e, and g) appears to be slightly more intense than for samples treated with the polymer solutions (Figure 11.2 b, d, and f). However, this result can not be verified as changes in fluorescence intensity along the fiber was not measured in this study.

11.4.2 Scanning Electron Microscopy

The image of an untreated hair fiber (Figure 11.3a) shows the fiber to be undamaged as the cuticle scales are flat in a downward overlapping manner and have sharp edges. There appears to be a small amount of contamination present on this sample by dust particles which appear as brightly defined artifacts. When analyzed using backscattering, the dust particles emitted a scattering pattern while the fiber itself was essentially invisible.

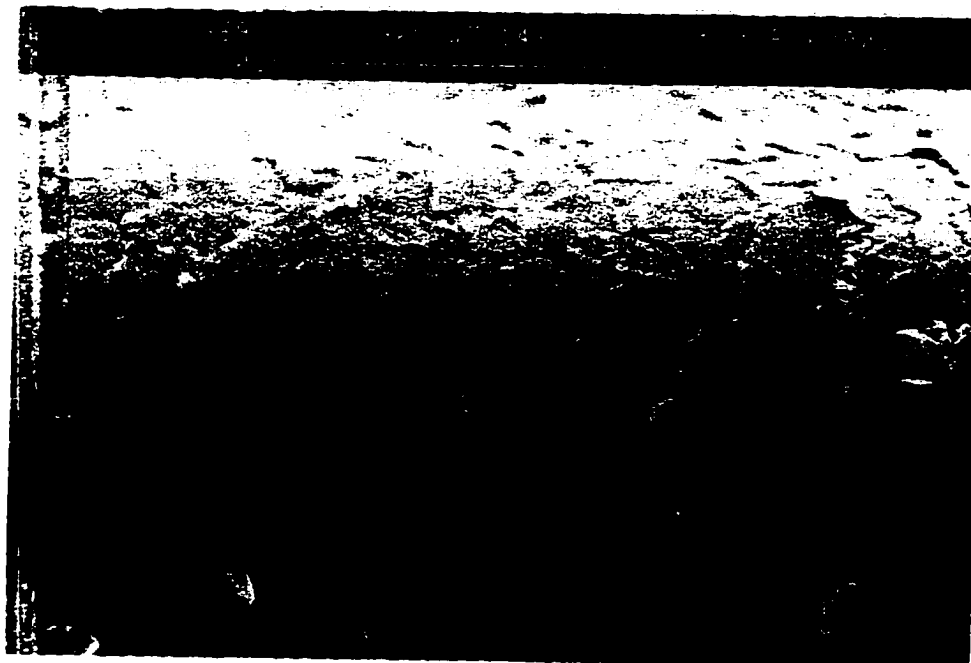
The fiber sample treated with 0.4% Polyquaternium 10 appears to be unevenly coated as seen by lotion like deposits (Figure 11.3b). These deposits run in a downward manner. Other portions of the fiber appear to be more homogeneously coated with the adsorbed polymer as evidenced by a softening of the cuticle scale edges in the upper portion of the image. The sample which was treated with 0.4% Polyquaternium 10 and 1% SDS also appears to be unevenly coated by the adsorbed polymer - SDS complex (Figure 11.3c). The evidence of uneven adsorption is the formation of rod-like crystals on the fiber surface which is easily seen in the bottom right of the image. The formation of these crystals may result from the strong binding of Polyquaternium 10 to the hair fiber. Polyquaternium 10 has been shown to bind strongly to keratin, and repeat applications result in soiling of the fiber due to buildup in deposit thickness.²⁰² This crystal formation may play a role in the difficulty in desorption of the Polyquaternium 10 -SDS complex from the fiber and may promote subsequent buildup (soiling) of the fiber by repeated adsorption at these sites.

Fiber samples treated with MQNED, MQNED - SDS, and DQNED appear to be uniformly coated with the adsorbed polymers and polymer - SDS complex (Figure

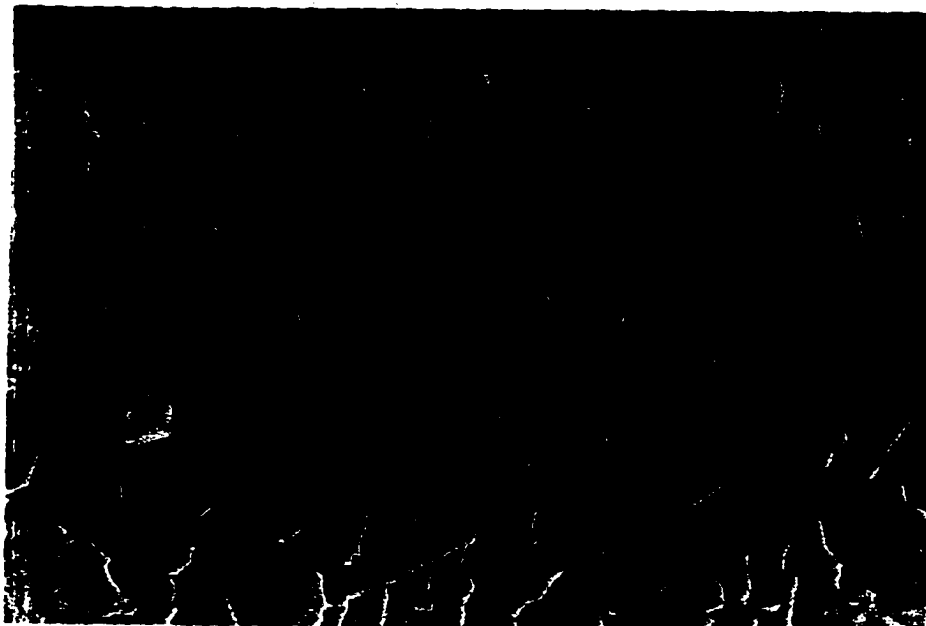
Figure 11.3: Characterization of the Deposition of Polymers on Hair Fibers Using Scanning Electron Microscopy

- (a) untreated hair fiber (control)**
- (b) hair fiber treated with Polyquaternium 10 (0.4% polymer)**
- (c) hair fiber treated with Polyquaternium 10 and SDS
(0.4% polymer, 1% SDS)**
- (d) hair fiber treated with MQNNED (0.4% polymer)**
- (e) hair fiber treated with MQNNED and SDS
(0.4% polymer, 1% SDS)**
- (f) hair fiber treated with DQNNED (0.4% polymer)**
- (g) hair fiber treated with DQNNED and SDS
(0.4% polymer, 1% SDS)**

(a)

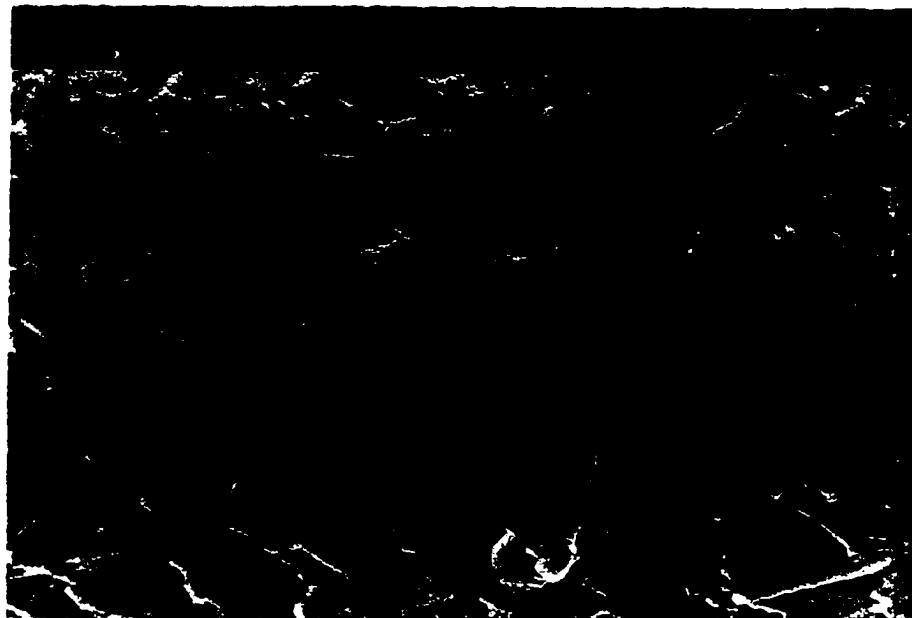


(b)

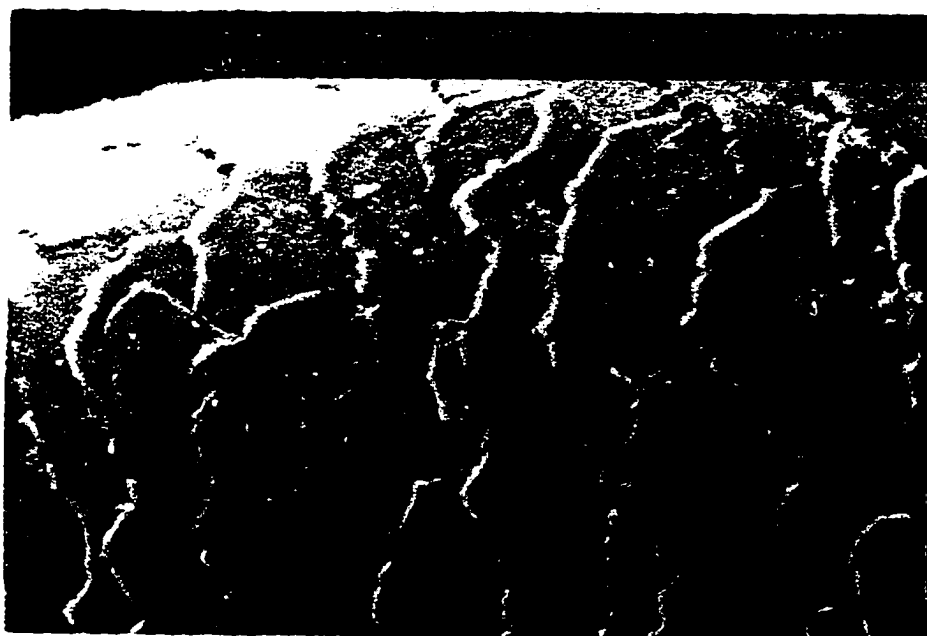


(Figure continued)

(c)



(d)

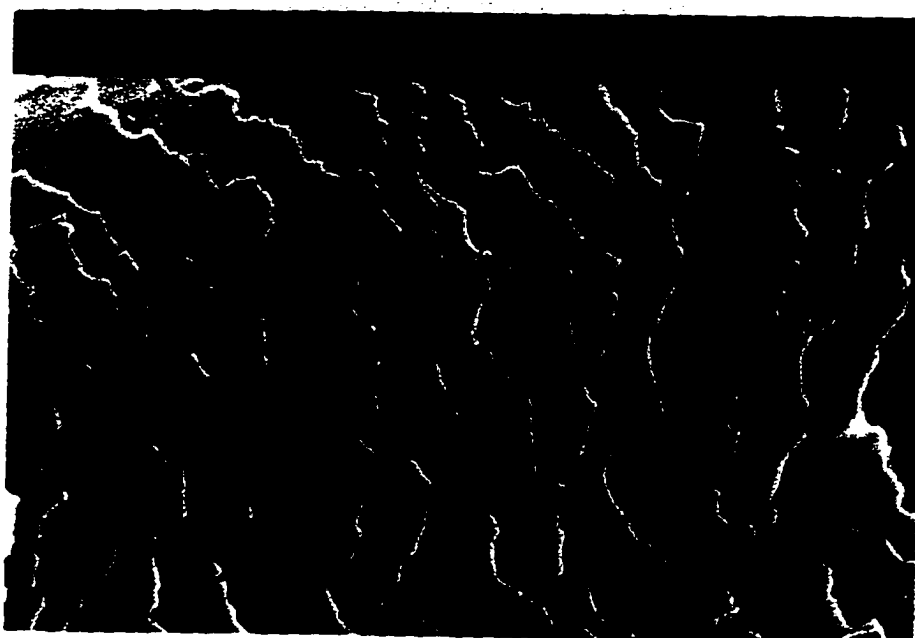


(Figure continued)

(e)

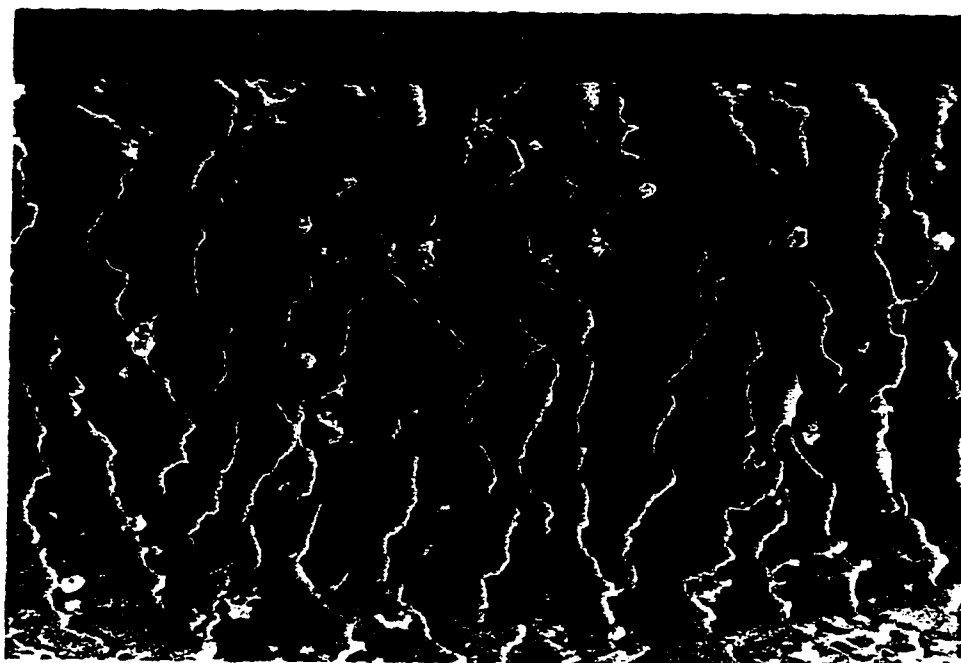


(f)



(Figure continued)

(g)



11.3d, e and f). Uniformity of the adsorbed layer is determined by a softening of the cuticle scale edges as compared with the untreated fiber. The hair fiber which was treated with DQNNED and SDS appears to be unevenly coated with the polymer-surfactant complex as bright artifacts appear in the image (Figure 12.3g). This artifact may be a result of the formation of DQNNED-SDS crystals or microgels which adhere to the fiber surface. Contamination of the sample by dust particles was ruled out as a possibility due to the uniformity of the artifact shape.

11.5 CONCLUSIONS

Epifluorescence microscopy and SEM show that the hair fibers are undamaged prior to treatment due to the uniformity of fluorescence intensity and appearance of the cuticle scales in the SEM images. Epifluorescence indicates that the fibers are homogeneously coated regardless of the treatment applied. However, SEM shows the

fibers treated with either Polyquaternium 10, Polyquaternium 10 - SDS, or DQNNED - SDS to be unevenly coated. The evidence of this inhomogeneity is the formation of lotion-like deposits, crystals and possibly microgels on the fiber surface. The fibers treated with either MQNNED, MQNNED - SDS, or DQNNED are uniformly coated with the adsorbed polymer or polymer - surfactant complex. The evidence of homogeneous adsorption is the uniform softening of the cuticle scale edges and absence of artifacts in the SEM images.

Future studies should include the determination of the nature or degree of surface modification of the fibers by the polymers and polymer - surfactant complexes, the film properties of the deposited resins, and the desorption characteristics of the polymers. Changes in fiber wettability should be determined as wettability affects the performance of the deposited resins. The hold performance of the resins and strength of the junctions formed should be investigated.

CHAPTER 12: CONCLUSIONS

We have prepared aminoalkylcarbamoyl cellulose derivatives where the amino functional group is still accessible to modification by quaternization. Quaternization with either iodomethane, or hydroxypropyl trimethylammonium chloride, or epichlorohydrin and dimethylamine yields water soluble polyquaternary ammonium salts of various degrees of quaternization. The solution properties of these compounds have been investigated in order to determine the utility in cosmetic formulation. Comparison of these quaternary aminoalkylcarbamoyl cellulosic and chitosan derivatives by viscosity indicates that the derivatives containing a low number of cationic charges per graft and shorter graft length have the highest viscosifying power. The diquaternary polymer, DQNNED, exhibited the highest viscosity of all the polymers studied. This high viscosity remained unaffected by the addition of increasing amounts of ethanol. These results indicate that DQNNED appears to be a potential improvement over Polyquaternium 10 and the other monoquaternary polymers studied. This effect may allow for lower concentrations of both polymer and ethanol to be utilized in cosmetic formulation. Future studies might include the effect of added low molar mass (LMM) electrolyte on the viscosity of these systems. Added electrolyte will screen the charges and should result in a reduction of viscosity. The effect of valency of the added electrolyte on viscosity should also be investigated.

The interaction of mono and diquaternary aminoalkylcarbamoyl cellulose derivatives with sodium dodecyl sulfate was studied, and the behavior was compared with Polyquaternium 10. Solubility studies indicated that all three polymers precipitate at their respective theoretical charge neutralization ratios when the concentrations of

polymer and anionic surfactant are greater than 0.010%. However, at polymer concentrations less than 0.010%, a minimal fixed concentration of sodium dodecyl sulfate is necessary to precipitate the complexes. The magnitude of the fixed concentration decreases as the charge density of the polymer increases.

For the polymer - mixed surfactant micelle complexes studied, the critical mole fraction of anionic surfactant necessary to cause precipitation appears to be dependent upon both flexibility of the polyelectrolyte and the number of charges on the graft. Below the critical overlap concentration, a flexible polyelectrolyte will support a higher micelle charge density than a semi-rigid polyelectrolyte. Above the critical overlap concentration, where intermolecular interactions predominate, a monoquaternary polyelectrolyte will support a higher charge density than its diquaternary analog regardless of the flexibility of the polyelectrolyte.

Changes in the vibronic fine structure of the pyrene fluorescence intensity spectra indicated that the micellar regions formed in the polymer-surfactant complexes were more hydrophilic than micelles formed in the absence of polymer. This result is independent of polymer concentration. At low concentrations of polymer ($c < c^*$) and surfactant ($C_s > C_M$), this result is consistent with the concept of smaller micelles being bound along the polymer strand. For smaller micelles, one would expect the water penetration to be greater so that the pyrene would encounter more of the polar palisade layer of the micelle and the water associated with this layer. At high concentrations of polymer ($c > c^*$) and surfactant ($C_s \gg C_M$), the similar values of I_1/I_3 for both surfactant solutions and polymer - surfactant complex solutions indicate that the interiors of the polymer bound surfactant clusters and normal micelles have almost equal polarity.

The results of cumulant analysis of the polymers and polymer - surfactant complexes indicated that both the Polyquaternium 10 and Polyquaternium 10 mixed surfactant micelle systems were monodisperse. However, the systems of MQNNED, DQNNED, MQNNED mixed surfactant micelle and DQNNED mixed surfactant micelle complexes were polydisperse as determined from upward curvature in plots of the average decay rate *versus* q^2 at high q . Temperature studies indicated that the aqueous solution of Polyquaternium - mixed surfactant micelle complex exhibited a different temperature response than polymer - mixed surfactant micelle complexes formed with polymers synthesized in our laboratories. Therefore, polymer structure may play a role in aggregation phenomena of the polymer - mixed surfactant micelle complexes.

Plots of surface tension *versus* surfactant concentration show evidence of three interaction zones corresponding to formation of the surface active complex, precipitation of the complex due to adsorption of a monolayer of surfactant monomer, and resolubilization of the complex. The interaction zones are present regardless of polymer structure or charge density. The ability of the polymer - surfactant complex to reduce surface tension appears to be independent of polymer architecture and dependent only upon adsorption of the surfactant species at the cationic polymer sites.

Foam studies indicated that the system containing Polyquaternium 10 requires more polymer to produce maximal foamability of SDS than does either MQNNED or DQNNED. Therefore, polymers containing a cationic charge closely associated to the polymer backbone will show improvements in initial foamability of SDS solutions. Although these solutions produce the maximum initial foam height, they are not the most stable over time. A greater amount of SDS is required for the solutions to produce a

stable foam. At the higher concentration of SDS, polymers containing a single cationic charge closely associated to the polymer backbone exhibit the most stable foams as the second cationic charge per graft appears to reduce foam stability.

Future studies of the interaction of these polyquats with surfactants should include the use of turbidimetric techniques to determine solubility as certain compositions may produce microemulsions which would be impossible to detect otherwise. Microscopy should be used to investigate the systems which formed gels as liquid crystal systems may be present. The addition of LMM electrolyte and effect of LMM valency should be studied as addition of salt weakens the binding of the polymer to the surfactant and should produce changes in the phase diagram. Emulsions should be made and the mechanism of emulsification should be determined both above and below the critical overlap concentration.

The results of an antimicrobial activity study indicate the dual role that quaternary polymers may have in cosmetic products. They potentially may be used as thickeners or conditioners, and they may also exhibit antimicrobial activity in the preservation of the cosmetic products. The hydroxypropyl trimethylammonium chitosan chloride derivative appears to be bactericidal while the aminoalkylcarbamoyl cellulose derivative, DQNNED, appears to be only bacteriostatic. The exact difference between these two compounds is not completely understood at this point in time but should be investigated. We believe that it is either a molecular weight effect or the presence of the carbamoyl moiety in the DQNNED polymer. The chitosan derivative has a starting molecular weight of approximately 100,000 g/mol. Whereas the DQNNED has a starting molecular weight of 250,000 g/mol. This difference in molecular weight may

allow a higher concentration of CHI-Q188 to be adsorbed on the cell membrane thereby increasing the efficacy of this compound. The carbamoyl moiety is electron attracting, therefore, it may reduce the efficacy of this derivative. More work in this area should be done in order to investigate the effects of molecular weight, degree of quaternization, and inclusion of electron releasing or attracting groups on the efficacy of these compounds. The safety of these polymers should be tested using mammalian cell cultures and eventually *in vivo* test methods to determine irritancy potential for humans. Future work would involve attaching either drugs or agricultural chemicals to utilize these derivatives as polymer carriers.

Future studies of keratin affinity should include determination of nature or degree of surface modification of fibers by the polymers and the film properties of the deposited resins. Changes in fiber wettability should be determined as wettability affects the performance of hair sprays. The hold performance of the resins and strength of the junctions formed should be investigated. Deposition of the resins on fibers should be visually determined in order to assess degree of fiber mending.

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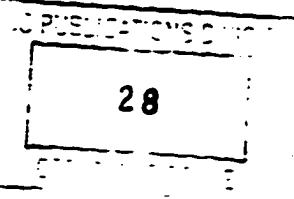


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Melissa Ann Manuszak was born on January 5, 1969 in Parma, Ohio. She attended Green Valley Elementary and St. Columbkille schools to complete her primary education in 1983. Then, she attended Padua Franciscan High School in Parma, Ohio, and graduated in 1987. Her next four years were spent attending Miami University in Oxford, Ohio. She graduated in 1991 with a bachelor of science degree in Chemistry and a minor area in Music Performance. That same year, Melissa enrolled in the College of Pharmacy at The University of Cincinnati to pursue studies in the cosmetic science program. In 1993, she completed a year of internship at L & F Products, Montvale, New Jersey. This experience enabled her to complete the master of science degree in Pharmaceutical Science at The University of Cincinnati in 1993. Upon completing her master's degree, Melissa entered Louisiana State University and began studies for a doctorate in chemistry. On July 16, 1994, Melissa married Vincent François Guerrini of Paris, France, and they currently reside in Baton Rouge, Louisiana. Melissa is currently a candidate for the degree of doctor of philosophy in the Department of Chemistry, and her area of specialization is Polymer Science.

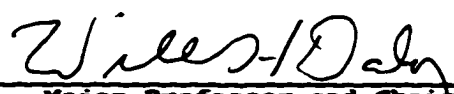

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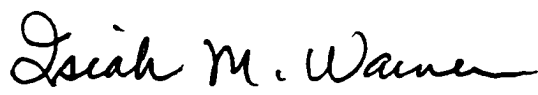

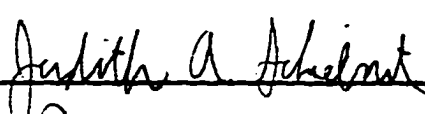

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